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# Technique for in situ Calibration of Particulate Mass Monitors

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# Technique for In Situ Calibration of Particulate Mass Monitors

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For calibrating stack beta gauges, larger aerosol output of 5-10 mg is needed, requiring a valve with a metering volume at least ten times larger than present valves. Contact electrification monitors require a test aerosol of 25 $mg/m^3$ at a flow of 1 $m^3$/min. Appropriate for this application is the ultrasonic nebulizer, which has an output of 50 mg/min, constant to within 8% over a period of hours.

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# TECHNIQUE FOR IN SITU CALIBRATION OF PARTICULATE MASS MONITORS

by

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## ABSTRACT

Two types of aerosol generators, the Riker Laboratories metered spray can and the Mistogen EN145 ultrasonic nebulizer, were evaluated by laboratory measurements for application to the in situ calibration of particulate mass monitors for stationary sources. The metered spray can delivers a fixed amount of aerosol each time the valve is depressed. The average mass of propellant and solution in each squirt is 52 mg, and is reproducible within 4%. The total volume of the dried particles per squirt is of the order of $10^{-5} cm^3$. The volume median diameter was varied from 1.4 to 3.2 μm by selection of solute concentration. Because of its simplicity and reproducibility of output, the metered spray may be useful for a variety of applications requiring a portable aerosol source. For calibrating stack beta gauges, larger aerosol output of 5-10 mg is needed, requiring a valve with a metering volume at least ten times larger than present valves. Contact electrification monitors require a test aerosol of 25 $mg/m^3$ at a flow of 1 $m^3/min$. Appropriate for this application is the ultrasonic nebulizer, which has an output of 50 mg/min, constant to within 8% over a period of hours.



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# SECTION 1

## INTRODUCTION

The objective of this project was to evaluate portable aerosol generators suitable for in situ calibration of stationary source particle mass monitors. There are two factors involved in the validity of stack measurements, (1) the degree to which the sample is representative of the stack effluent, and (2) the accuracy of the instrument response. With a portable aerosol generator of known output, the second question of instrument response could be answered in the field under typical operating conditions. This would be useful both for testing the monitor performance, and as part of the calibration of the monitor against the EPA Reference Method. The EPA Method 5 involves the collection of a stack sample with a filter and a series of impingers, which are later analyzed gravimetrically. The lack of immediate information from this method is a handicap in the calibrations of a continuous mass monitor. It would be desirable to know prior to the calibration whether the mass monitor is functioning properly, both to save time and to increase the reliability of the calibration.

In this project aerosol generators were evaluated in terms of the calibration requirements for two types of continuous mass monitors, the beta absorption gauge, and the contact electrification monitor. For the beta gauge the particulate matter is accumulated for a few minutes on a filter followed by a mass determination via the absorption of beta particles from a radioactive source. The contact electrification monitor senses the electrical charge transfer taking place when particles impact on a probe; this charge is proportional to the mass. The calibration requirements for these two monitors are outlined in Section 3. Aerosol generators appropriate to each were evaluated, as described in Sections 4 and 5. A third common type of monitor, the optical transmissometer, measures the light attenuation produced by particulate matter. This type of monitor presents a different calibration problem than the beta absorption or the contact electrification monitor and was not included in the scope of the present project.

## SECTION 2

## CONCLUSIONS AND RECOMMENDATIONS

In this study, two types of aerosol generators, the metered spray can and the ultrasonic nebulizer were investigated for use in the field as a test aerosol source.

The metered spray can produces a fixed amount of aerosol each time the valve is depressed. To be useful for instrument calibration, the generated aerosol must be reproducible. The size distribution and total mass delivered should be appropriate to the instrument being tested. For metered sprays using a 50 mg valve from Riker Laboratories, the total dried particle volume is of the order of $10^{-5}$ $cm^3$. The volume median diameter varies from 1.4 to 3.2 μm for solute concentrations of 0.1 to 3%. The particle volume per squirt for each of the cans tested has a coefficient of variation between 6% and 29%. However, the mass of propellant and solution in each squirt is reproducible within 4%. Some of the greater variability in the volume is attributed to measurement error. At higher solute concentrations, the measured dried particle volume is significantly less than expected. The discrepancy is attributed to higher losses for the larger particles. Variation in these losses would also contribute to the variation in particle volume.

The best results were obtained with low solution concentration. For a spray composed of 0.1% benzoic acid in a 30% ethanol, 70% Freon-12 solution, the aerosol produced with each squirt has a volume of $1.7 \times 10^{-5}$ $cm^3 \pm 10\%$ and a mass median diameter of $1.40 \pm 0.05$ μm. Both the reproducibility and the size distribution of this aerosol are appropriate for testing stack beta gauges, but a greater mass per squirt is needed. Because of aerosol losses, increasing the solute concentration is not an effective means of obtaining a larger mass output. To obtain sufficient mass for the stack beta gauge a valve with a metering volume at least ten times larger is required; this appears to be feasible.

For applications which require of the order of 10 μg of aerosol, spray cans using the present metered valves would be suitable. The can weight loss measurements show the valve output is reproducible within 4%. Further development would be needed to avoid particle losses. Improvements in aerosol volume consistency will not come from improvement in the valve, but probably from reduction of particle losses. Smaller particle sizes would be helpful in avoiding losses. For some applications, a submicron aerosol is needed. These smaller particles could be produced by using a more dilute aerosol solution.

The Mistogen ultrasonic nebulizer produces a large, continuous amount of aerosol. For a nebulizing solution of 0.033 g/ml of potassium biphthalate in water, an output of 50 mg/min with a mass median diameter of 1.4 μm was measured. Aerosol volume and size distributions are constant, within experimental error, over a period of several hours. This generator is appropriate for testing the contact electrification monitor.

This study has shown that the metered spray can and the ultrasonic nebulizer have sufficiently reproducible output to be used as test aerosol generators. The present metered spray cans are appropriate for applications requiring about 10 μg of particles. A valve with a larger metering volume is needed to supply the 5-10 mg of aerosol required for the stack beta gauges. The ultrasonic nebulizer, with a large continuous output, could be used for the contact electrification monitor. The use of these aerosol sources in the field will require provision of portable dilution systems. This will be relatively easy to accomplish for the spray can but somewhat more difficult for the ultrasonic nebulizer because of the large volume required. The metered spray can, because of its simplicity and consistent output, could find a variety of other uses as a portable particle generator.

## SECTION 3

## REQUIREMENTS OF AN AEROSOL SOURCE FOR CALIBRATING MASS PARTICULATE MONITORS

This study is concerned with the in situ testing of particulate mass monitors for stationary sources. A portable aerosol generator is to be used to calibrate the sensor. The question of representative sampling is not addressed. The test aerosol need not have the properties of the source particles. Also, it is not intended that the sampling efficiency of the monitor should be measured. Basically, a portable aerosol generator is required to deliver a test aerosol of a known concentration or total mass to the monitor.

The aerosol size distribution and mass loading must be appropriate for the monitor to be tested. To formulate the requirements for the aerosol generator, a survey was made of commercially available beta gauge and contact electrification mass monitors.

### BETA GAUGE MASS MONITORS

Beta gauges provide continuous or semi-continuous monitoring of airborne particulate mass loadings (1-5) and for stack sampling, beta gauges have been extensively used in Europe. Lear Siegler advertises that their instrument has been used in over 90 European installations. To date, use in this country is limited. However, in a survey of measurement methods for particulate emissions from combustion sources, Gilmore Sem, et al. (6) rated the beta gauge as having the greatest immediate potential for continuous stack particulate mass monitoring.

#### Principle of Operation

For beta particles of energies less than 1 MeV, the principal interaction with matter is inelastic scattering with the orbital electrons. The attenuation of the beta radiation passing through a material is a measure of the material's areal electron density. As the ratio of atomic number to atomic mass is 0.4 to 0.5 for most elements, the beta attenuation is a direct indication of the sample mass.

Empirically, the attenuation is given by the relation:

$$I = I_o e^{-\kappa\sigma}$$

where I and $I_o$ are the measured intensities of the $\beta$ radiation with and without the sample; and $\sigma$ is the mass per unit area of the sample. The

calibration constant $\kappa$ depends primarily upon the energy of the $\beta$-source. Most samplers use $^{14}C$, which has a maximum $\beta$ emission energy of 0.156 MeV, and a 5700 year half life. For this isotope, the constant $\kappa$ is about 0.26 $cm^2/mg$.

To measure the airborne particulate mass, particles are deposited on a surface; the intensities of the beta radiation which penetrates the collection substrate before and after aerosol collection determine the mass per unit area of the deposited particles. Typically, samples are collected with a filter, but some beta gauges use an electrostatic precipitator (7) or an impactor stage. (8) It is not feasible to use beta gauging in situ, e.g., to observe attenuation directly across a stack, because the attenuation will be dominated by that of the gas phase mass, which is of the order of $10^3 g/m^3$, far exceeding particulate loadings.

## Commercial Beta Gauge Stack Monitors

In the United States, continuous stack mass monitors using the beta gauging principle were manufactured by Research Appliance Corporation (R.A.C.) and Lear Siegler (L.S.). Currently, only R.A.C. is actively marketing the device.

Table 1 lists the operational and design parameters of these two stack mass monitors. Both devices collect the aerosol onto a filter tape. Lear Siegler uses a glass fiber filter, whereas R.A.C. uses the Whatman No. 4 paper filter. Both companies use a carbon-14 beta source and a Geiger Mueller tube detector. The intensity of the beta radiation penetrating the filter is measured on the same spot both before and after the sample collection. This method eliminates error due to variation in filter thickness along the tape. The filter mass is of the order of 5 to 10 $mg/cm^2$, whereas the collected particle mass is in the range of 0.2 to 5 $mg/cm^2$.

TABLE 1. COMMERCIAL BETA GAUGES FOR STACK MONITORING

| | Research Appliance Co. | Lear Siegler |
|---|---|---|
| Beta Source | < 100 μCi $^{14}C$ | < 100 μCi $^{14}C$ |
| Detector | Geiger Mueller Tube | Geiger Mueller Tube |
| Type of Filter | Cellulose (Whatman #4) | Glass Fiber |
| Sample Spot Area | 5 $cm^2$ | 9 $cm^2$ |
| Sampling Rate (including dilution air) | < 0.1 $m^3$/min (< 4 CFM) | 0.06-0.2 $m^3$/min (2-6 CFM) |
| Sample Time | Variable: limits no specified | Variable 0.5 to 50 min |
| Count Time | 60 sec | 50 sec |
| Average Count Rate | 50,000 $min^{-1}$ | 20,000 $min^{-1}$ |
| Range of Filter Loadings | > 2 mg | 2 to 50 mg |
| Operating Conditions for Beta Gauge | Ambient Temp. Low RH (Dew Pt = -40°C) (purge with dry air) | Ambient Temp. & RH Sample Line Heated, 170°C |

For both of these commercial instruments, the sample flow rates and probe diameters are variable, chosen to obtain approximately isokinetic sampling. Sample times are adjusted to obtain a mass deposit within the working range of the instrument. There is a dead time, i.e., no sampling, while the filter tape is being counted. Differences between the two instruments in the sample collection, dilution, cooling and flow measurement are described below.

Research Appliance Company Sampling System

The R.A.C. employs a stationary probe, positioned in the stack at a point where the effluent velocity equals the average stack velocity, as determined by a pitot tube survey. Upon the initial setup, the sampler is calibrated against EPA Method 5 to determine that the R.A.C. monitor is correctly positioned to obtain a representative sample.

Condensation is avoided by using a sample line which can be heated to 120°C. A boundary layer diluter introduces dry (dew pt = -40°C) air along the walls of the sample tube to reduce the relative humidity and temperature and to lower wall losses. After the particles have been filtered, the diluted sample gas stream passes through a condenser to remove water vapor, and then the dry air volume is monitored. The input dilution air is also measured, the difference of the two measurements used to determined the actual sample volume. The company specifies there are no losses of particles below 7 μm diameter. Their beta gauge is designed to be operated downstream of a bag house or electrostatic precipitator, to monitor performance of these devices. The company states that at this point in the stack most of the larger particles have been removed.

Lear Siegler Sampling System

Lear Siegler uses a swiveling probe, designed to sweep out equal areas in equal time in the stack. The flow rate is held constant, sampling velocity is set either equal to, or 10% greater than the average stack effluent velocity. To avoid condensation in the sample line, heating collars are used to maintain a constant temperature as high as 170°C. An optional attachment permits the addition of dilution air to the sample stream. The sample air flow is measured by monitoring the differential pressure across a venturi nozzle downstream of the filter. Ideal gas laws are used to correct the flow to standard conditions. Unlike the R.A.C. instrument, this sample volume will include volume due to water vapor.

The requirements for a calibration aerosol for beta gauges are listed in Table 2.

TABLE 2. REQUIREMENTS OF CALIBRATION AEROSOL SOURCE FOR THE BETA GAUGE MONITOR

| | |
|---|---|
| Type of aerosol | solid |
| Particle size | < 7 μm |
| Total mass delivered | 5-10 mg |
| Time dependence | No restrictions |
| Flow rate | 0.06 $m^3$/min |

## CONTACT ELECTRIFICATION MASS MONITORS

In monitoring instruments based on contact electrification, a flow of the aerosol is directed at a probe. The transfer of charge from particle-probe collisions results in a current which is continuously monitored with a sensitive meter. The electrical charge correlates accurately with the mass determined gravimetrically for a given source material. The physical principles and the operating characteristics of the monitor have been reviewed by John. (9,10)

Two instruments are currently available commercially, the IKOR Continuous Particulate Monitor, IKOR Division, OMNI-WAVE Electronics Corporation, Gloucester, Massachusetts, and the KONY TEST, Kony Co., Ltd., Tokyo, Japan. The current number of units in the field is not known, but is probably less than 100. The characteristics of the two instruments are listed in Table 3. The concentration range for the IKOR can vary somewhat depending on the probe configuration, the probe material and the material sampled. Both instruments are equipped with an in-line filter which affords a gravimetric sample for calibration purposes.

TABLE 3. COMMERCIAL CONTACT ELECTRIFICATION MASS MONITORS

| | IKOR | KONY TEST |
|---|---|---|
| Type of sampling | Extractive or in situ | Extractive |
| Sensor configuration | Streamlined or turbulent | Tube |
| Sensor material | Metal | Semiconductor |
| Sampling rate | 0.5-0.9 $m^3$/min (17-30 CFM) | 0.15-1.0 $m^3$/min (5.3-35 CFM) |
| Concentration range | 0.2 mg/$m^3$-230 g/$m^3$ | 0.1 mg/$m^3$-8 g/$m^3$ |

The calibration of the contact electrification monitors must take into account a special problem, namely that the instrument requires equilibration for a period of from several minutes up to 15 or 20 minutes. During this time the sensitivity varies, approaching an asymptotic value as the surface of the probe is conditioned in the aerosol stream. The calibration procedure would consist of exposing the probe to the calibration aerosol until the current signal reaches its steady state. Then the current would be integrated over a convenient period of time, say five minutes, to obtain the charge to be related to the mass of sampled aerosol. If the test aerosol were aluminum oxide, for example, approximately 25 mg/$m^3$ will give a reasonable current signal. Calibration of the contact electrification monitor requires a non-sticky aerosol. The particle size distribution should have a substantial fraction above 0.1 μm diameter since the particles are sensed by impaction on the probe.

The desirable characteristics of a calibration aerosol source are listed in Table 4.

TABLE 4. REQUIREMENTS OF CALIBRATION AEROSOL SOURCE FOR THE CONTACT ELECTRIFICATION MONITOR

| | |
|---|---|
| Type of aerosol | Non-sticky solid |
| Particle size | > 0.1 μm diameter |
| Concentration | > 25 $mg/m^3$ |
| Time dependence | Constant within 10% for 30 minutes |
| Flow rate | 1 $m^3/min$ |

## SECTION 4

## EVALUATION OF METERED SPRAY CANS

Metered spray cans were investigated as a means of producing a test aerosol for the beta gauge monitors. In reporting this work we use the term aerosol strictly to refer to a suspension of liquid or solid particles in a gaseous medium, and not to the spray can itself.

Instead of a continuous spray, the metered cans deliver a fixed quantity of aerosol each time the valve is pressed. Metered sprays are used commercially for dispensing bronchial sprays to relieve symptoms of asthma. The questions of interest in terms of their applicability as a test aerosol for particulate monitors are: (1) the reproducibility of the mass per spray, (2) the particle size distribution, and (3) the total mass obtainable with each spray. To test the beta gauges used for stack monitoring 5 to 10 mg of an aerosol less than 7 μm particle diameter is required.

### PRELIMINARY WORK; COMMERCIAL METERED SPRAYS

Three commercially available metered bronchial sprays, Isuprel (Winthrop Laboratories), Primatene (Whitehall Laboratories) and Bronitin (Whitehall Laboratories), have been investigated. These are each equipped with a 50 mg metered valve, U.S. Patent No. 2968427, manufactured by Riker Laboratories (Northridge, CA). The Bronitin differs from the Isuprel and Primatene in that the concentrate is a suspension rather than a solution. Each of the cans uses a Freon propellant.

A diagram of the metered valve is shown in Figure 1a. The small reservoir between the stem and the surrounding cylinder is filled through a groove in the bottom of the stem when the valve is closed. Depressing the valve stem first seals the small reservoir from the bottle, and then opens it to the atmosphere through a 0.8 mm orifice at the top of the valve stem. There is a second 0.3 mm orifice in the actuator used to depress the stem (not shown). The two rubber gaskets which seal against the valve stem determine the upper and lower boundaries of the reservoir volume.

A similar metered valve which was inspected but not tested is shown in Figure 1b. This valve is manufactured in England by Metal Box Ltd., (Reading, England) and marketed in this country by Precision Valve Co., (Yonkers, New York). It is very similar in design to the Riker valve. The principal differences are (1) the major components of the valve are plastic, rather than metal, (2) communication with the bottle when the valve is closed is by means of grooves in the side of the reservoir volume.

## Experimental Methods for Preliminary Testing of Commercial Spray Cans

As shown in Figure 2 the aerosol was introduced into a 4 cm diameter glass pipe. The spray can is held in an inverted position, to insure proper functioning of the metered valve. A transit time down the pipe of approximately 4 seconds allows the propellant to evaporate. Aerosol is sampled with the Climet 208 optical particle counter, using the Climet dilution system to avoid coincidence losses. The dilution system operates by introducing a particle-free sheath air flow at the sampling inlet, equal to 99% of the total sampling rate of 7 lpm. The maximum count rate of the optical counter was $10^4$ per sec.

Particle size distributions were obtained from the Climet output pulses using a Nuclear Data Pulse Shape Amplifier, and Tracor Northern Multichannel analyzer. The data were recorded on paper tape and reduced by computer. The optical particle analyzer was calibrated using polystyrene latex spheres (Dow Diagnostics) and monodisperse glycerol particles generated with a Berglund-Liu vibrating orifice. Two amplifier gain settings were used, covering the particle size ranges from 0.40 to 2.0 μm, and 1.7 to 6.1 μm. A total number count was also obtained from an Ortec single channel analyzer and a counter/timer.

### Time Dependence

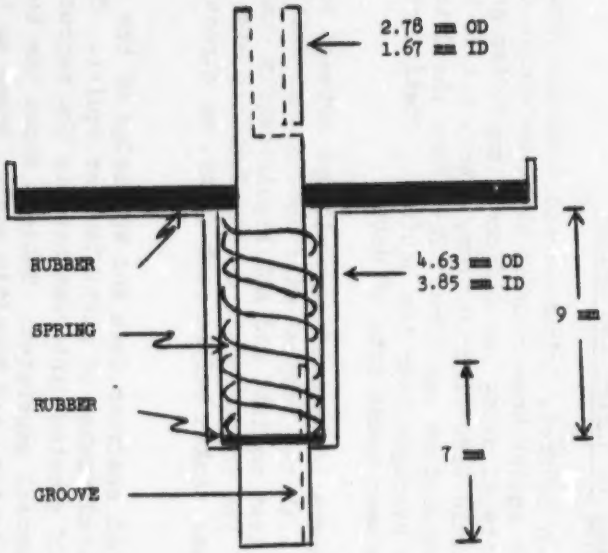
The time dependence of the particle count following a squirt of Isuprel was recorded on the multichannel analyzer operated in the multiscaler mode. An example is shown in Figure 3. The analyzer count rate has been adjusted for sample dilution. The aerosol number reaches a maximum of approximately $6 \times 10^6$/s in about one second, falling rapidly thereafter.

### Reproducibility of Particle Number and Volume

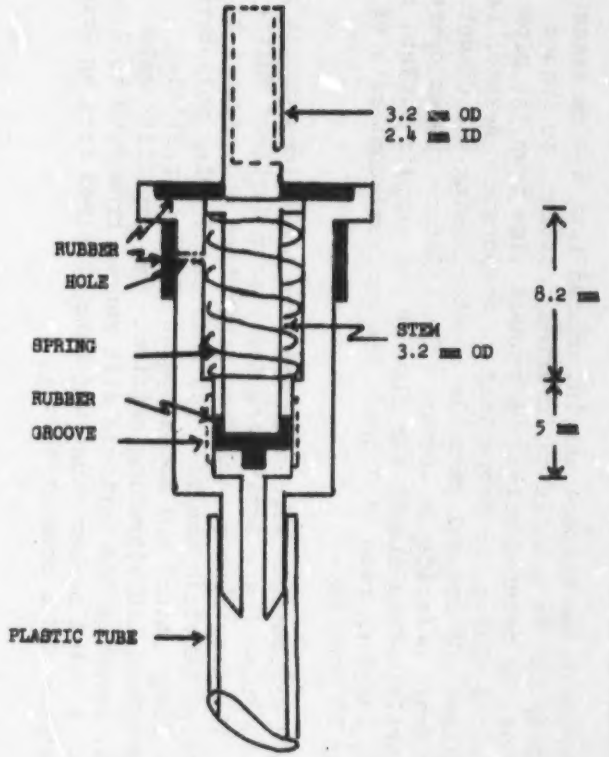
Data were taken on Isuprel, Primatene and Bronitin sprays. The number of particles from each squirt were counted with the single channel analyzer. Because of the necessity of using two different amplifier gain settings, only part of the particle size distribution, either 0.4 to 2.0 μm, or 1.7 to 6.1 μm could be measured at one time. Therefore the data taken in these two size regions were averaged over ten squirts. Statistics were obtained from the variation between these sets of data.

In these experiments 100 seconds was allowed between successive squirts of the can. Testing with the Isuprel mist showed that waiting longer, up to 20 minutes since the last squirt, did not significantly change the number of particles generated. For measurements on the Bronitin mist, which is a suspension, the can was shaken before each spray, as directed by the manufacturer.

The single channel analyzer data and knowledge of the flow rates allows calculation of the total number of particles per squirt. The results are listed in Table 5. Of greatest interest here is the reproducibility of the volume or mass, of aerosol generated. Table 6 shows the total aerosol number and volume for the Primatene and Bronitin mists, based on the pulse height




(a)




(b)

Figure 1. Commercial metered valves: (a) from Riker Laboratories; (b) from Precision Valve Company.

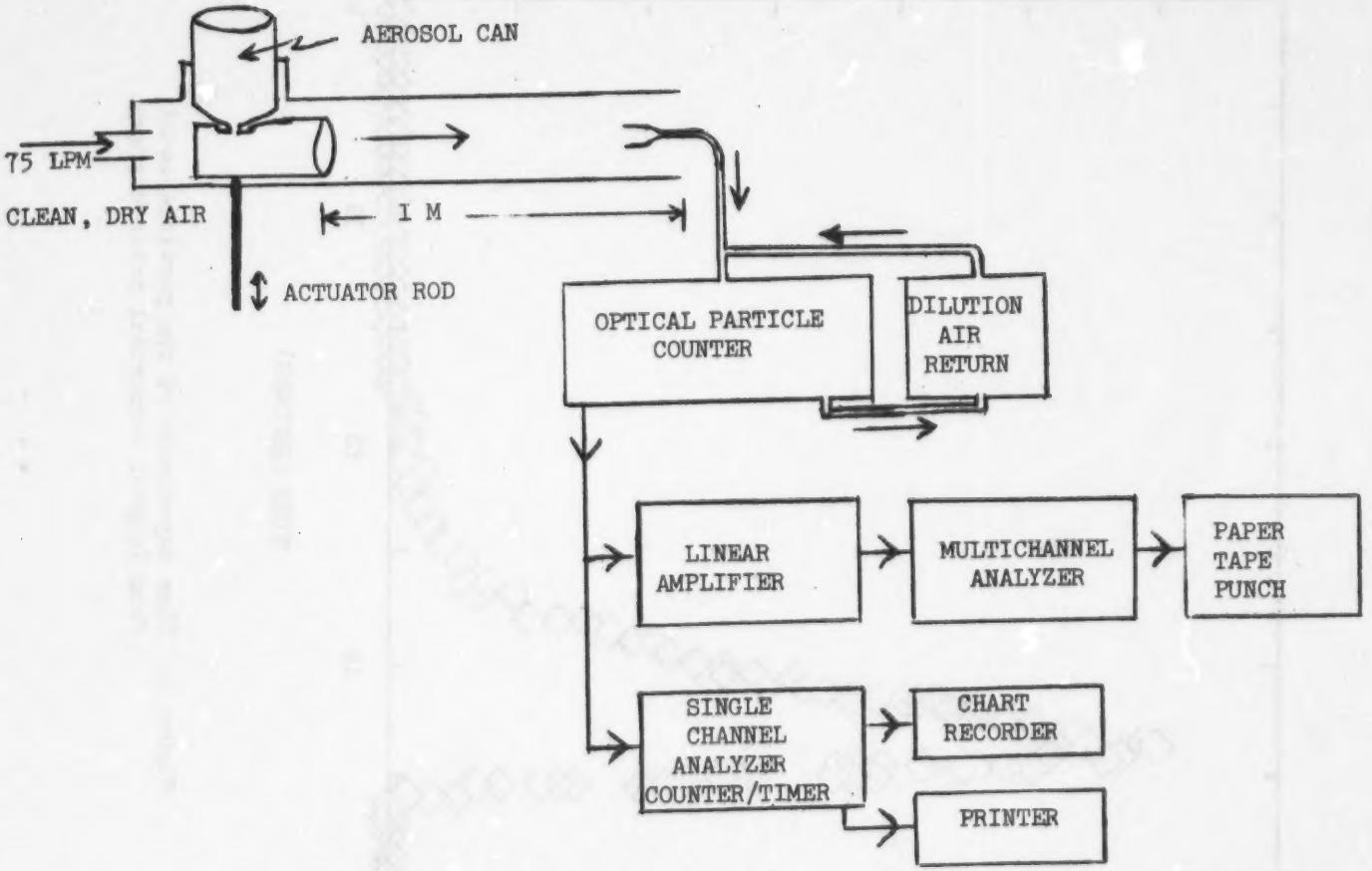



Figure 2. Sampling system for preliminary testing of commercial metered spray cans.

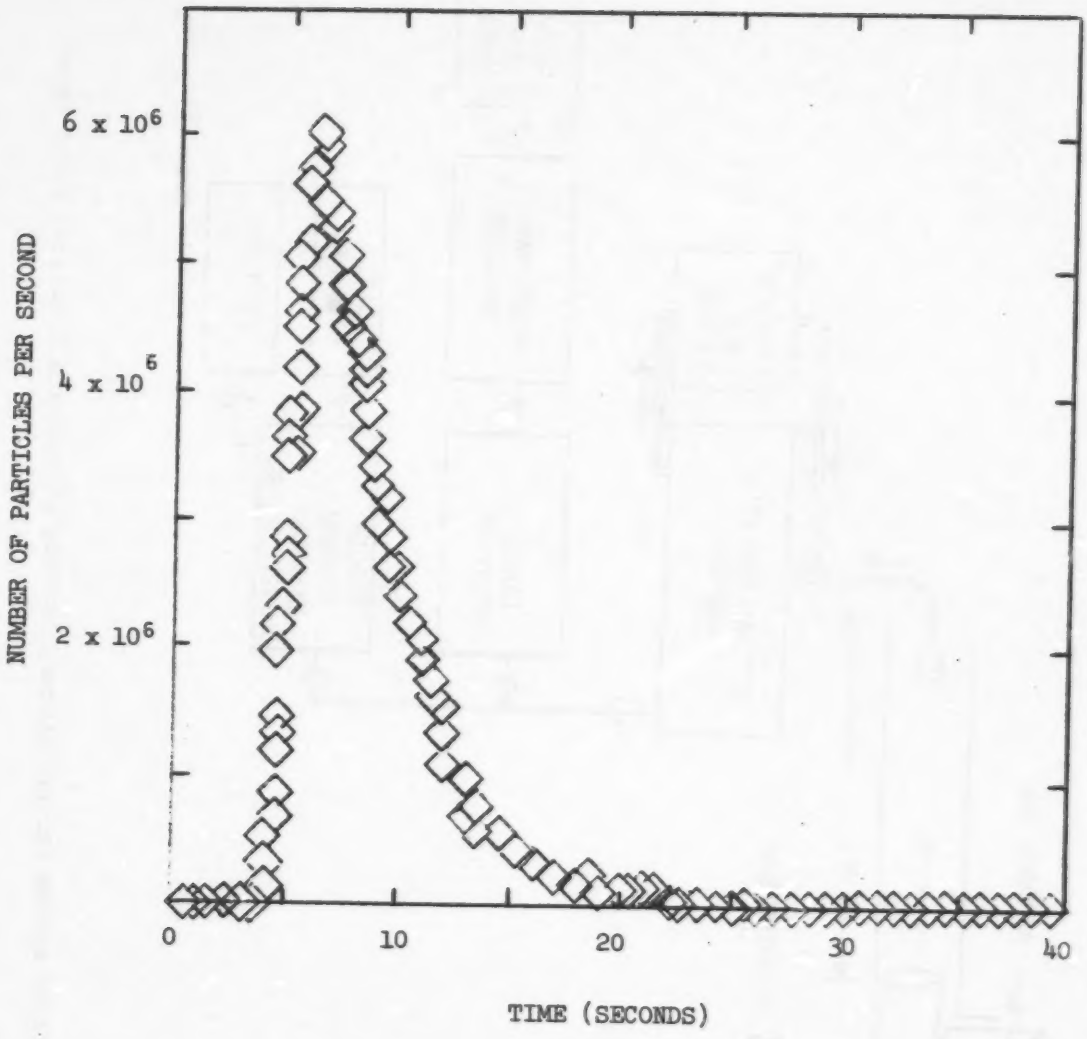



Figure 3. Time dependence of the particle count from Isuprel commercial metered spray.

analyzer data. The data are shown in two size ranges corresponding to the two amplifier gain settings used to span the entire particle size range. Each set of data is an average of 10 squirts of the aerosol can. The standard deviations are given for the data sets. The number data in Table 7 based on the multichannel analyzer counts are slightly smaller than the data in Table 6 which were derived from the single channel analyzer counts. The latter covered a slightly wider particle size range.

TABLE 5. NUMBER OF PARTICLES PER SQUIRT FROM COMMERCIAL SPRAYS

| | No. of Squirts | No. of Data Sets* | Average of Individual Squirts | Average of Data Set Averages |
|---|---|---|---|---|
| Isuprel | 67 | 5 | $4.43 \times 10^7 \pm 35\%$ | $4.26 \times 10^7 \pm 26\%$ |
| Primatene | | | | |
| Can #1 | 70 | 7 | $5.44 \times 10^7 \pm 33\%$ | $5.53 \times 10^7 \pm 17\%$ |
| Can #2 | 20 | 2 | $6.63 \times 10^7 \pm 30\%$ | --- |
| Can #3 | 52 | 5 | $4.37 \times 10^7 \pm 30\%$ | $4.35 \times 10^7 \pm 8.9\%$ |
| All cans | 142 | 14 | $5.13 \times 10^7 \pm 37\%$ | $5.15 \times 10^7 \pm 23\%$ |
| Bronitin | 60 | 6 | $8.97 \times 10^7 \pm 36$ | $8.97 \times 10^7 \pm 23\%$ |

*Each data set consists of 8-20 individual squirts.

TABLE 6. PARTICLE NUMBER AND VOLUME PER SQUIRT FOR PRIMATENE AND BRONITIN COMMERCIAL METERED SPRAYS

| Primatene | No. of Data Sets | N | V ($\mu m^3$) |
|---|---|---|---|
| 0.40 - 2.1 μm | 7 | $4.41 \times 10^7 \pm 18\%$ | $1.11 \times 10^7 \pm 22\%$ |
| 2.1 - 6.1 μm | 7 | $9.51 \times 10^5 \pm 23\%$ | $7.66 \times 10^6 \pm 28\%$ |
| Total | | $4.51 \times 10^7 \pm 17\%$ | $1.88 \times 10^7 \pm 17\%$ |
| Bronitin | | | |
| 0.40 - 2.1 μm | 3 | $7.51 \times 10^7 \pm 21\%$ | $2.49 \times 10^7 \pm 11\%$ |
| 2.1 - 6.1 μm | 3 | $2.09 \times 10^6 \pm 8\%$ | $1.98 \times 10^7 \pm 7\%$ |
| Total | | $7.72 \times 10^7 \pm 20\%$ | $4.47 \times 10^7 \pm 7\%$ |

TABLE 7. PRIMATENE PARTICLE NUMBER AND VOLUME PER SQUIRT

| Amount in Can | N | V ($\mu m^3$) |
|---|---|---|
| Full | $4.5 \times 10^7 \pm 17\%$ | $1.88 \times 10^7 \pm 17\%$ |
| Half full | $4.47 \times 10^7$ | $1.27 \times 10^7$ |
| Quarter full | $4.04 \times 10^7$ | $1.13 \times 10^7$ |
| Within 5% of empty | $2.0 \times 10^7$ | No data |

The Primatene shows an overall 17% standard deviation in the number and in the volume between the data sets. The Bronitin mist, while showing a large deviation (20%) in the number of particles per squirt, has a smaller variation (7%) in the total aerosol volume. Thus the variation in the particle number is not necessarily a good measure of the variation in the particle volume. The data also show that the volume per squirt is about twice as large for Bronitin as for Primatene.

One of the Primatene cans was used until it emptied, which required about 300 squirts. The number of particles did not drop noticeably until the bottle was less than half full, as can be seen in Table 7. On the other hand the volume per squirt dropped by about 30% when the bottle was half full.

Discussion

The metered spray can shows promise as a portable aerosol calibration source. The particle size distribution is appropriate. The coefficients of variation for sets of 10 squirts were found to be 7% and 17% for Bronitin and Primatene, respectively. The volume dropped about 30% when the can was half full. These variations were small enough to justify further exploration of this approach.

PREPARED METERED SPRAYS

Because of the promise shown by commercial sprays, metered cans were prepared with our own test solutions. The concentration of the solution was varied to determine the effect on the total aerosol volume and the size distribution. Solutions of benzoic acid in ethanol, with concentrations of 3 mg/ml, 20 mg/ml and 100 mg/ml were packaged 30% w/w in Freon propellant.

Benzoic acid was chosen because it is highly soluble in ethanol and in Freon; thus a homogeneous solution could be obtained. 50 mg solution valves were obtained from Riker Laboratories; the solutions were packaged by Aerosol Services Inc., (425 S. Ninth Avenue, City of Industry, California 91745).

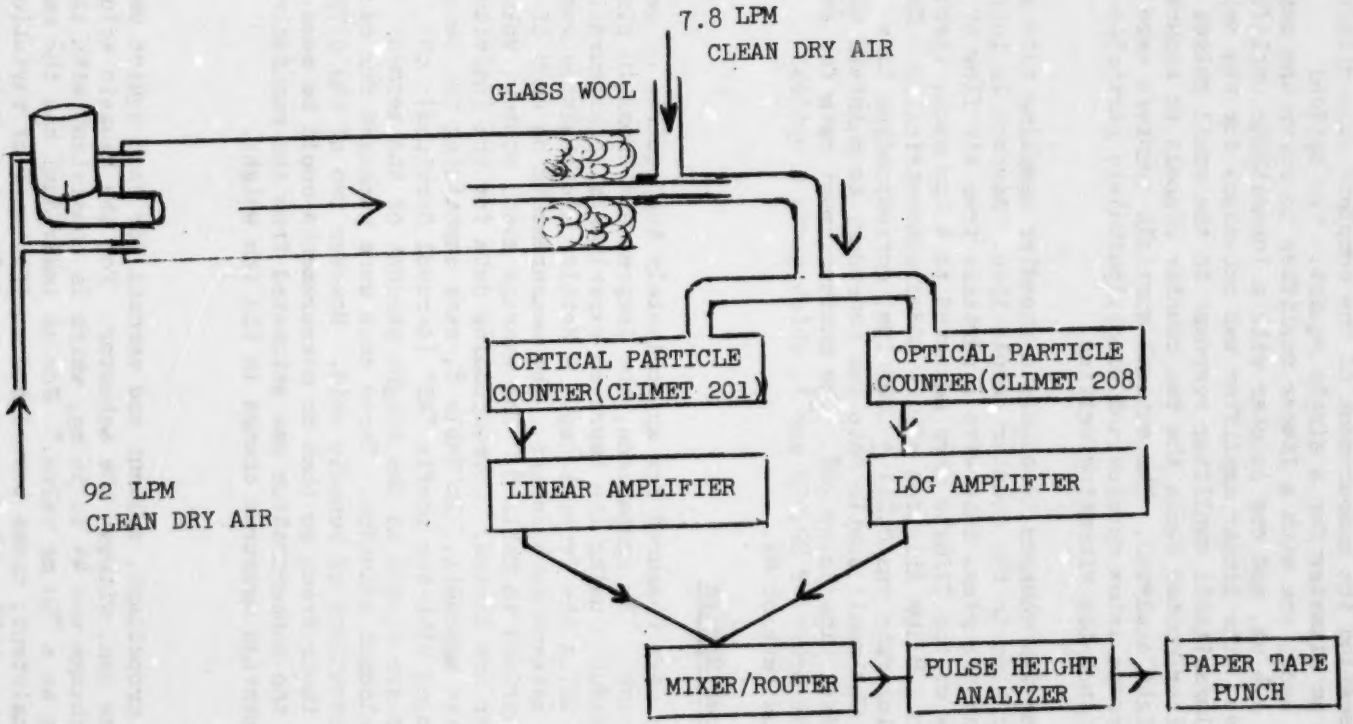



Figure 4. Sampling system to measure size distributions of prepared metered sprays.

## Experimental Methods for Prepared Sprays

The experimental set up is shown in Figure 4. The addition of a Tracor Northern mixer/router enabled the measurement of the complete size distribution from 0.4 to 7.8 μm diameter for a single squirt. Two optical particle counters were used, one with a linear amplifier to cover the small particle range, 0.4 to 1.4 μm, and one counter with a logarithmic amplifier to span the larger sizes. The linear amplifier was necessary for the small particle sizes as the logarithmic amplifier response to the small pulses was inadequate. The mixer/router sends the two counter signals to separate halves of the pulse height analyzer. The optical particle counters were calibrated with polystyrene latex spheres and dioctylphthalate particles generated with the Berglund-Liu vibrating orifice.

The dilution system was changed to obtain a steadier sampling rate and to minimize the transit time in the counter sample line. Aerosol is introduced into a 9.5 cm diameter glass tube with a particle free air flow of 92 lpm. The flow rates of the Climets were adjusted to 4 lpm each, through a 0.95 cm tube to which 7.8 lpm dilution air is added concentrically. The measured aerosol sampling rate was 0.211 $\pm$ .003 lpm, corresponding to a 436:1 dilution ratio. The small sample rate was necessary to maintain the multichannel analyzer dead time below 20%. The maximum count rate for each of the squirts is of the order of 20,000 $sec^{-1}$, which gives a optical counter coincidence loss rate of 6%.

## Measurements for Prepared Sprays

Size distributions were measured for approximately ten squirts of each of the prepared spray cans. For comparison, the Isuprel and Bronitin size distributions were remeasured using the improved experimental configuration. The cans were actuated using the Isuprel cap. A Mettler microbalance was used to weigh the cans between each squirt. The measurements on each of the spray cans are summarized in Table 8. The average mass, number, volume and mass median diameter are listed. Corresponding data for the individual squirts are listed in the appendix. In Table 8, cans containing the benzoic acid solutions are labeled with the prefix "AS" (Aerosol Services); the solution concentrations are listed as the weight percent of the aerosol material in the Freon-alcohol solution. Three cans were packaged for each of the different concentrations of benzoic acid. However two of the 0.7% solutions lost most of their Freon so that no measurements could be made. For the Bronitin spray the concentration was estimated from the manufacturers stated dosage and our average measured change in the can weight.

## Aerosol Volume

The total mass of propellant, solvent and aerosol for each squirt was measured by weighing the can, without the actuator. For the benzoic acid cans the average mass change was 44 to 56 mg, which is consistent with the manufacturers labelling as a "50 mg valve." For an individual can the mass per squirt is quite consistent; those tested had coefficients of variation of 1-8%, the average being 4.0%. These numbers are indicative of the performance of the valve itself, and do not include any losses in the actuator.

TABLE 8. METERED SPRAY CAN OUTPUT PER SQUIRT

| Can | Solution | Total Propellant and Aerosol Solution Mass (mg/squirt) | Particle Number (per squirt) | Dry Particle Volume ($cm^3$/squirt) | Volume Median Diameter (μm) |
|---|---|---|---|---|---|
| A.S. #1 | 0.1% Benzoic Acid | 55.9 ± 2.0% | $3.37 \times 10^7$ ± 10% | $1.96 \times 10^{-5}$ ± 8.6% | 1.4 ± .06 |
| A.S. #2 | 0.1% Benzoic Acid | 53.5 ± 4.4% | $3.51 \times 10^7$ ± 4.8% | $2.01 \times 10^{-5}$ ± 11% | 1.4 ± .05 |
| A.S. #3 | 0.1% Benzoic Acid | 51.2 ± 1.7% | $2.04 \times 10^7$ ± 7.7% | $1.17 \times 10^{-5}$ ± 6.2% | 1.4 ± .05 |
| A.S. #5 | 0.7% Benzoic Acid | 44.5 ± 5.4% | $2.1 \times 10^7$ ± 27% | $2.1 \times 10^{-5}$ ± 29% | 2.2 ± .1 |
| A.S. #7 | 3% Benzoic Acid | 51.4 ± 3.7% | $1.75 \times 10^7$ ± 8.7% | $2.8 \times 10^{-5}$ ± 19% | 3.1 ± .2 |
| A.S. #8 | 3% Benzoic Acid | 53.5 ± 2.5% | $1.94 \times 10^7$ ± 8.1% | $4.2 \times 10^{-5}$ ± 19% | 3.1 ± .2 |
| A.S. #9 | 3% Benzoic Acid | 53.7 ± 8.2% | $2.07 \times 10^7$ ± 5.5% | $4.54 \times 10^{-5}$ ± 11% | 3.2 ± .1 |
| Isuprel | 0.25% Isuprel hydrochloride | 56.7 ± 6.7% | $1.87 \times 10^7$ ± 9.3% | $1.58 \times 10^{-5}$ ± 13% | 2.0 ± .05 |
| Bronitin | ~0.5% epinephrine bitartrate | 62.9 ± 1.0% | $7.1 \times 10^7$ ± 15% | $5.3 \times 10^{-5}$ ± 18% | 1.6 ± 0 |

The aerosol volume (dried particles) is calculated from the optical particle counter size distributions. As shown in Table 8, the volume is of the order of $10^{-5}$ $cm^3$ per squirt. Neglecting losses it should also be possible to calculate the volume from the solution concentration, aerosol density, and weight loss of the can. However the aerosol volume derived from the optical counter is considerably smaller than that derived from the mass loss as shown in Table 9. The discrepancy is greater for the more concentrated solutions. For 0.1% benzoic acid the volume is almost half of the calculated value whereas for the 3% solution it drops to about 3% of the calculated number. The total number of particles detected decreases for the higher solution concentrations, also indicating more aerosol losses for the larger particles.

TABLE 9. RATIO OF THE AEROSOL VOLUME FROM THE OPTICAL COUNTER TO THAT DERIVED FROM MASS LOSS

| Can No. | Solution Concentration | Optical Counter Volume / Volume from Mass Loss |
|---|---|---|
| AS1 | 0.1% | 0.50 |
| AS2 | 0.1% | 0.51 |
| AS3 | 0.1% | 0.29 |
| AS5 | 0.7% | 0.075 |
| AS7 | 3% | 0.024 |
| AS8 | 3% | 0.036 |
| AS9 | 3% | 0.038 |
| Isuprel | 0.25% | 0.17 |
| Bronitin | ~0.5% | 0.23 |

Of importance in the application of these spray cans as test aerosol generators is the reproducibility of the aerosol output. As stated above, the mass of propellant and solution lost from the can with each squirt is 52 mg with an average coefficient of variation for an individual can of 4%. The total dry particle volume, based on optical counter measurement, was more variable. For the benzoic acid cans, the pooled coefficient of variance in the measured volume is 9.8% for the 0.1% solution, and 16% for the 3% solutions. The can AS #5, with a 0.7% solution, exhibited an anomalously high coefficient of variation of 29%. Unfortunately the other two cans prepared at this concentration were not functional. Some of the increased variation can be attributed to the larger errors inherent in the volume measurement, such as small fluctuations in air flows or sampling rates. Another source of variation is deposition and resuspension of solute in the actuator. Especially for the higher concentration cans, deposits were observed visually at the orifice in the actuator. Significant aerosol losses are also indicated by the discrepancy between the measured and calculated dry particle volume. These losses can contribute to variations in the aerosol volume which are not reflected in the can weight loss measurements.

For one of the cans, AS #1, measurements were made at successive stages as its contents were exhausted. Figure 5 shows the total mass of propellant and solution per squirt as a function of the number of squirts from the can. The mass is quite constant until the can is nearly empty after 200 squirts. The dry particle volume, shown in Figure 6 is not quite as steady, but shows the same sharp decrease around 200 squirts.

Size Distributions

Typical number and volume distributions for individual squirts of the benzoic acid solutions are shown in Figures 7, 8 and 9. The volume distributions have peaks at 1.5, 2.7 and 4 μm for benzoic acid concentrations of 0.1, 0.7 and 3% respectively. The volume distributions are very reproducible as seen by the small standard deviation in the volume median diameter (Table 8). The cumulative volume distributions, Figure 10, are approximately log normal for the two lower concentration solutions, but not for the 3% solution. Shown in Figures 11 and 12 are the Isuprel and Bronitin size distributions. The Isuprel is similar to the benzoic acid sprays in that the active ingredient is dissolved in the alcohol and the Freon propellant. The Bronitin is a suspension of solid particles with a surfactant in the Freon. Both of the commercial sprays have size distributions which are approximately log normal (Figure 13), with volume median diameters of 2.0 and 1.6 μm for the Isuprel and Bronitin respectively. The volume distribution for the Bronitin spray is distinctly narrower.

For the benzoic acid and Isuprel sprays the particle volume is expected to be linearly dependent on solution concentration, with a zero intercept. In Figure 14 the average volume per particle is plotted against solution concentration. The slope of the line on this log-log graph is only about 0.3. Also shown is the increase in volume median diameter with solution concentration. The reason for particle size not scaling with solution concentration as expected is not known; however, it may be related to particle loss, which is size-dependent.

In comparison with these sprays, the Bronitin has a larger aerosol volume with a relatively small mass median diameter of 1.6 μm. Because it is a suspension rather than a homogeneous solution, its size distribution is expected to depend on 1) particle size in the suspension and 2) the extent of coagulation in the spray.

DISCUSSION

The metered spray can holds promise as an inexpensive, portable aerosol calibration source. The output of the metered valve, as determined by can weight loss, is reproducible within 4%. The volume of aerosol produced by the lower concentration solution of 0.1% benzoic acid is reproducible within 10%. The performance of the more highly concentrated solutions is not as good, probably due to losses of the larger particles.

The size distribution meets the criteria stated in Section 3 for the beta gauges, namely that the aerosol be less than 7 μm. The aerosol mass produced by the metered cans is 25 to 60 μg per squirt, depending on the solution concentration. This is considerably less than the 5-10 mg needed

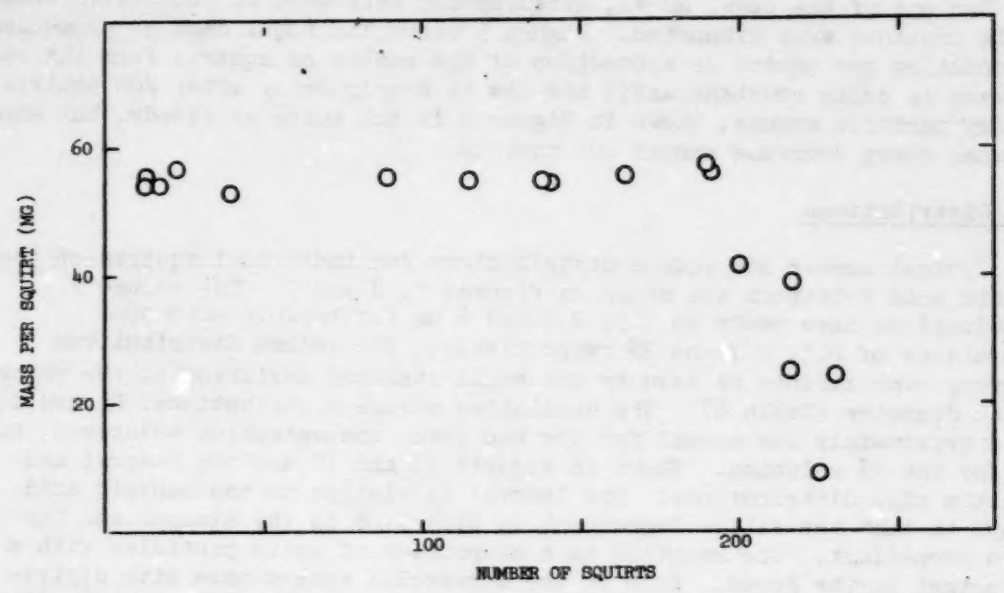



Figure 5. Propellant and solution mass output of 0.1% benzoic acid spray as the can is emptied.

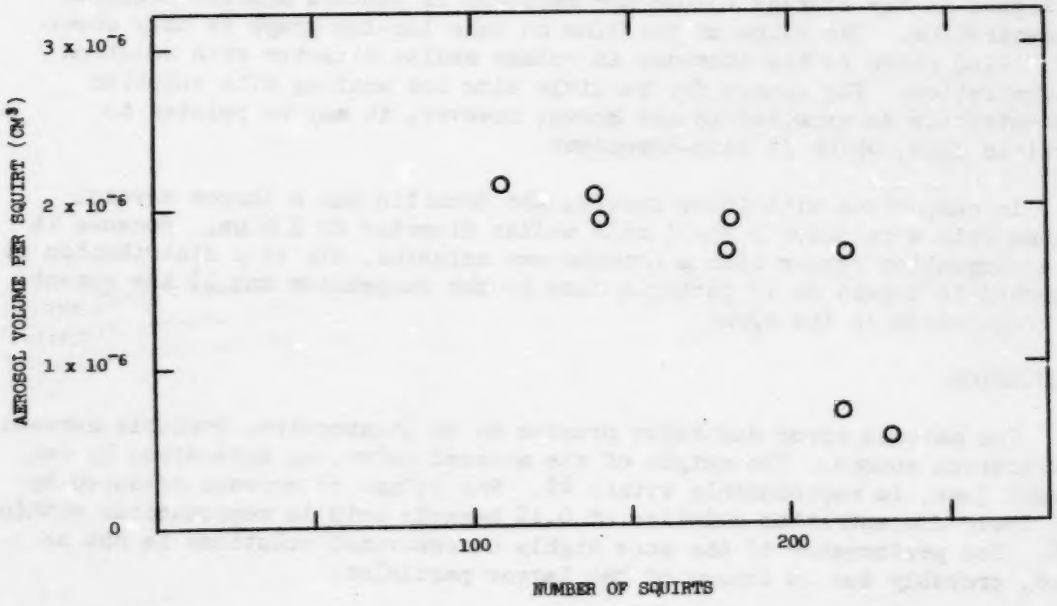



Figure 6. Particle volume of 0.1% benzoic acid spray as the can is emptied.

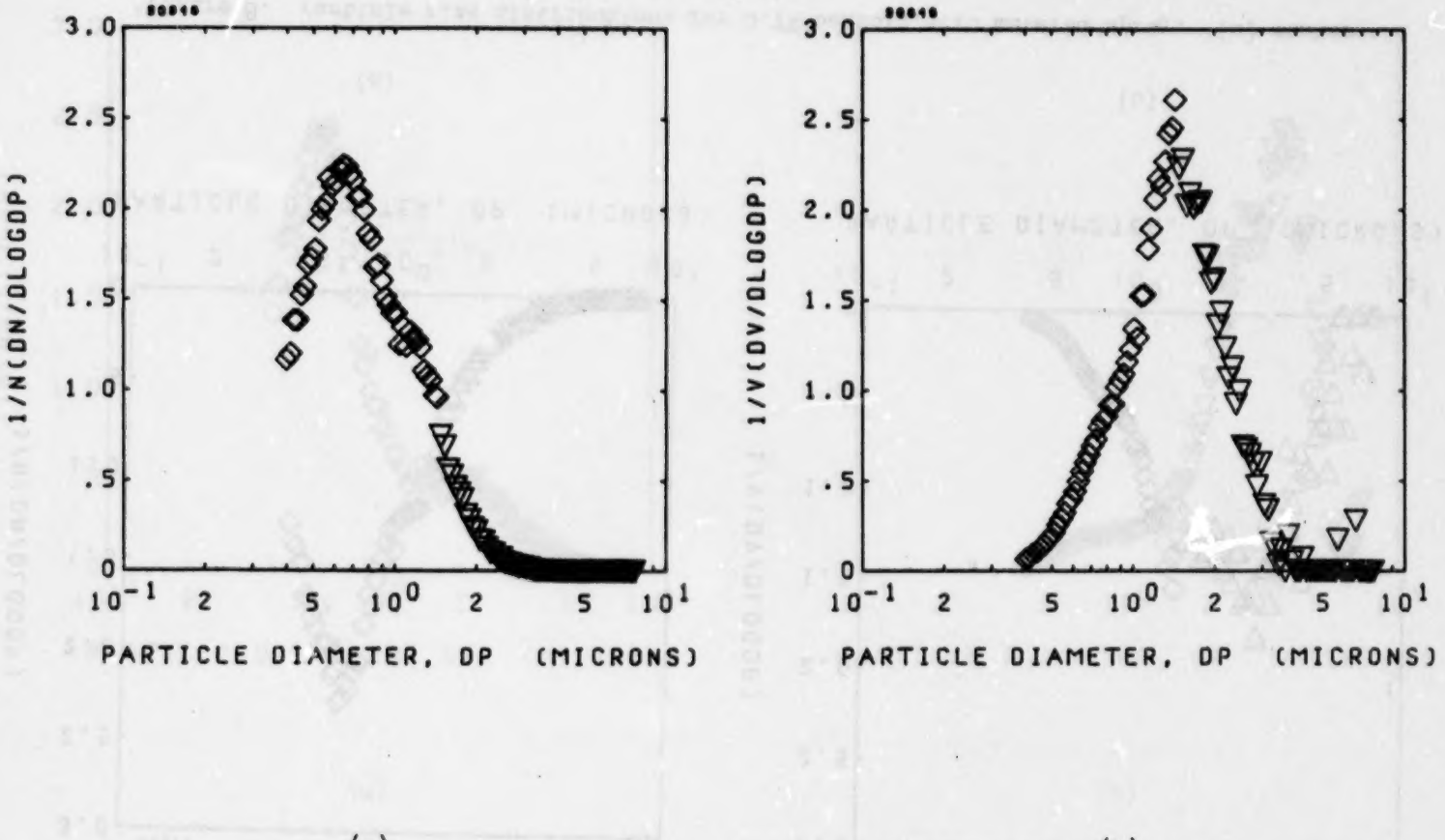
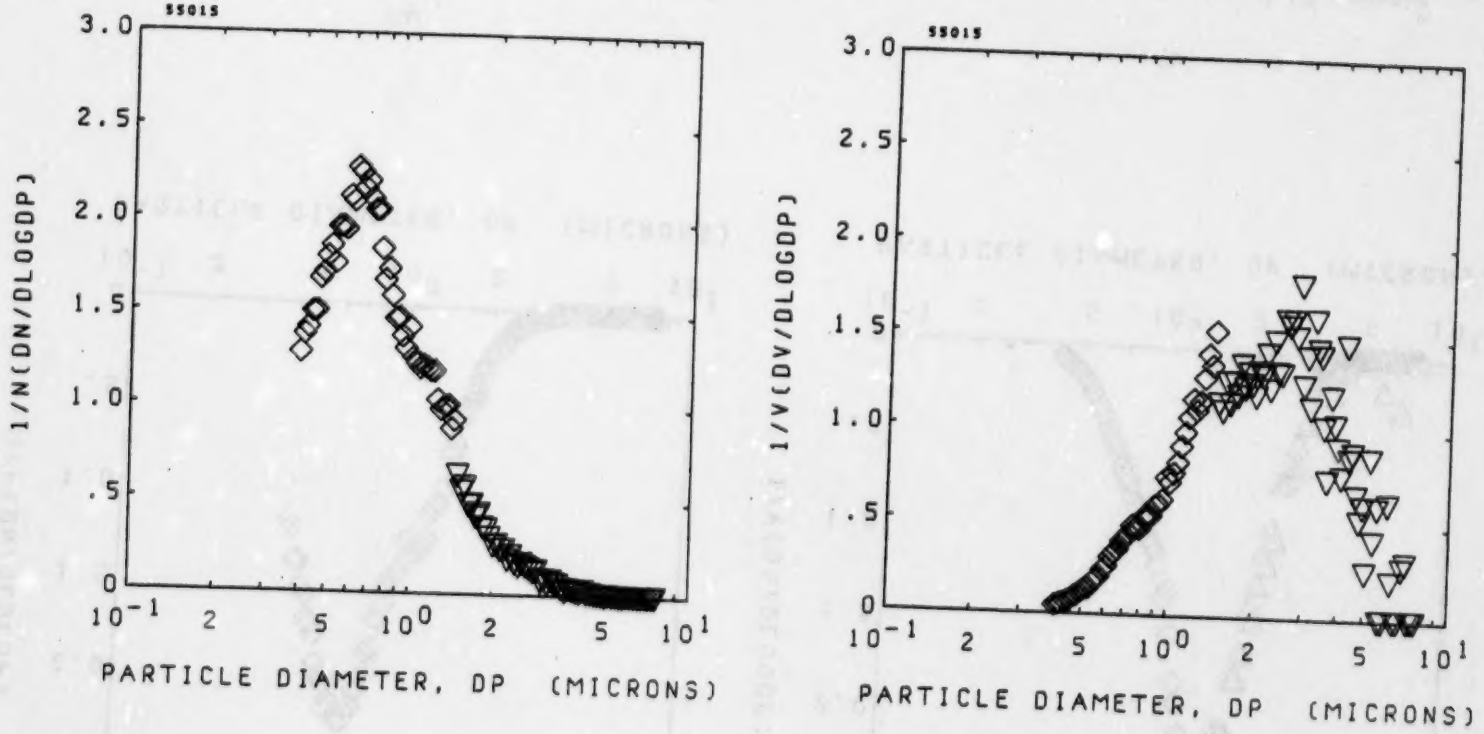



Figure 7. Particle size distributions for prepared metered spray containing 0.1% benzoic acid: (a) number distribution; (b) volume distribution. Data from the two particle counters are indicated by the symbols ◊ and ▽ .




(a) (b)

Figure 8. Particle size distributions for 0.7% benzoic acid metered spray: (a) number distribution; (b) volume distribution.

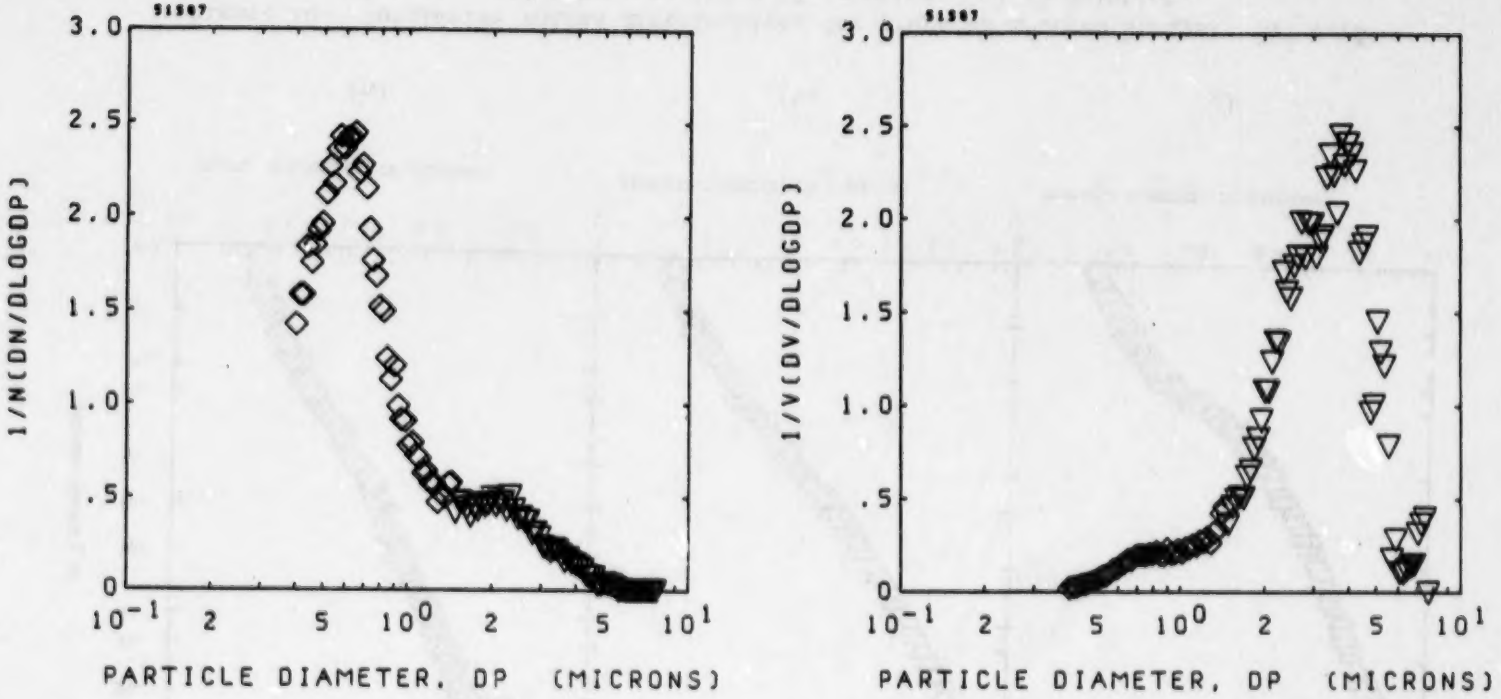



Figure 9. Particle size distributions for 3% benzoic acid metered spray: (a) number distribution; (b) volume distribution.

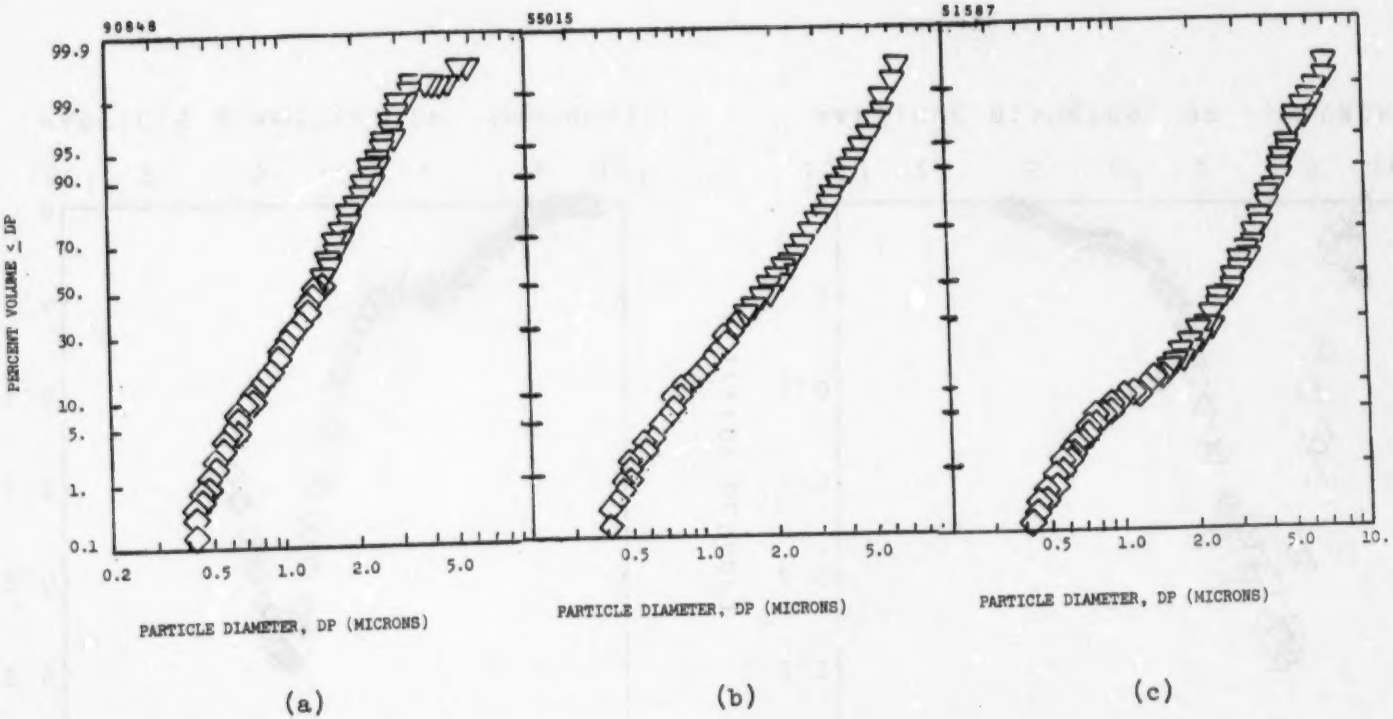



Figure 10. Cumulative volume distributions for prepared metered sprays: (a) 0.1% benzoic acid solution; (b) 0.7% solution; (c) 3% solution.

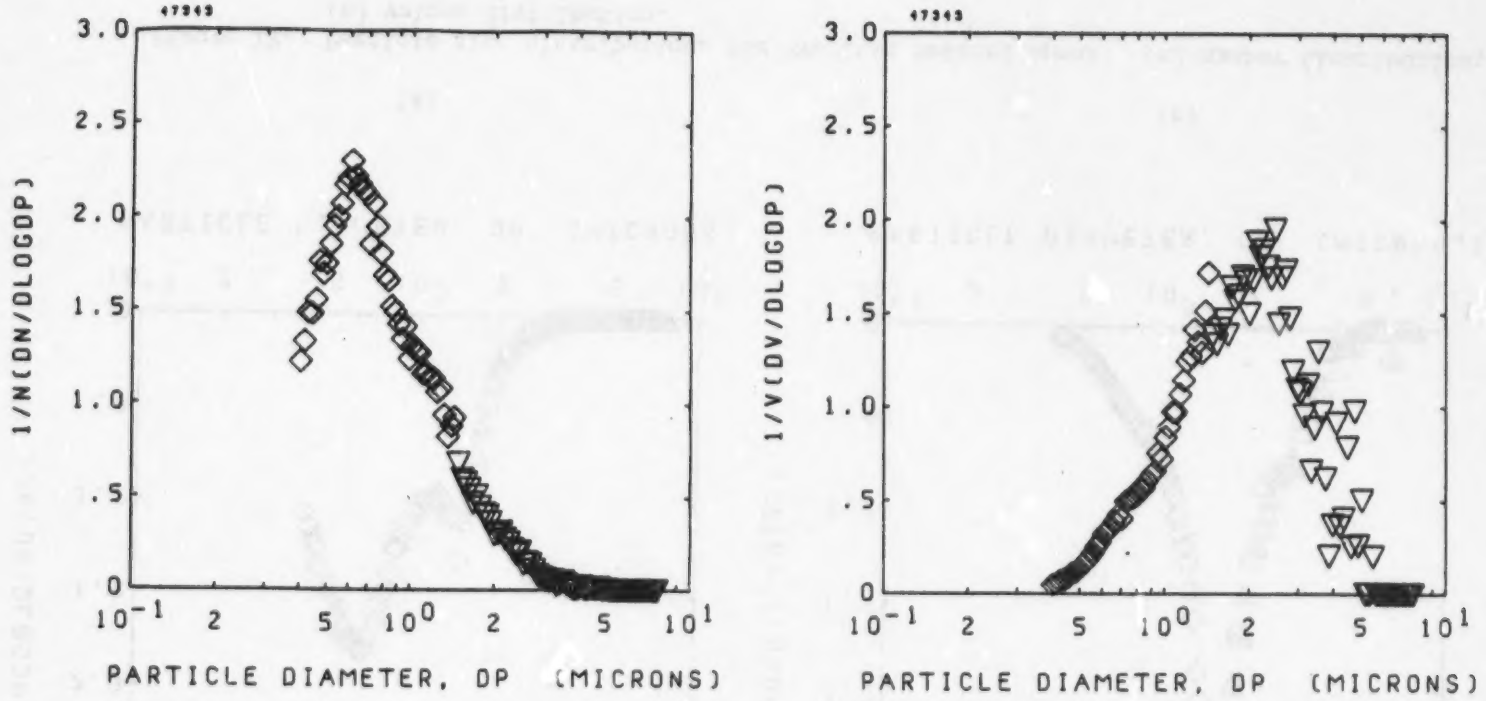
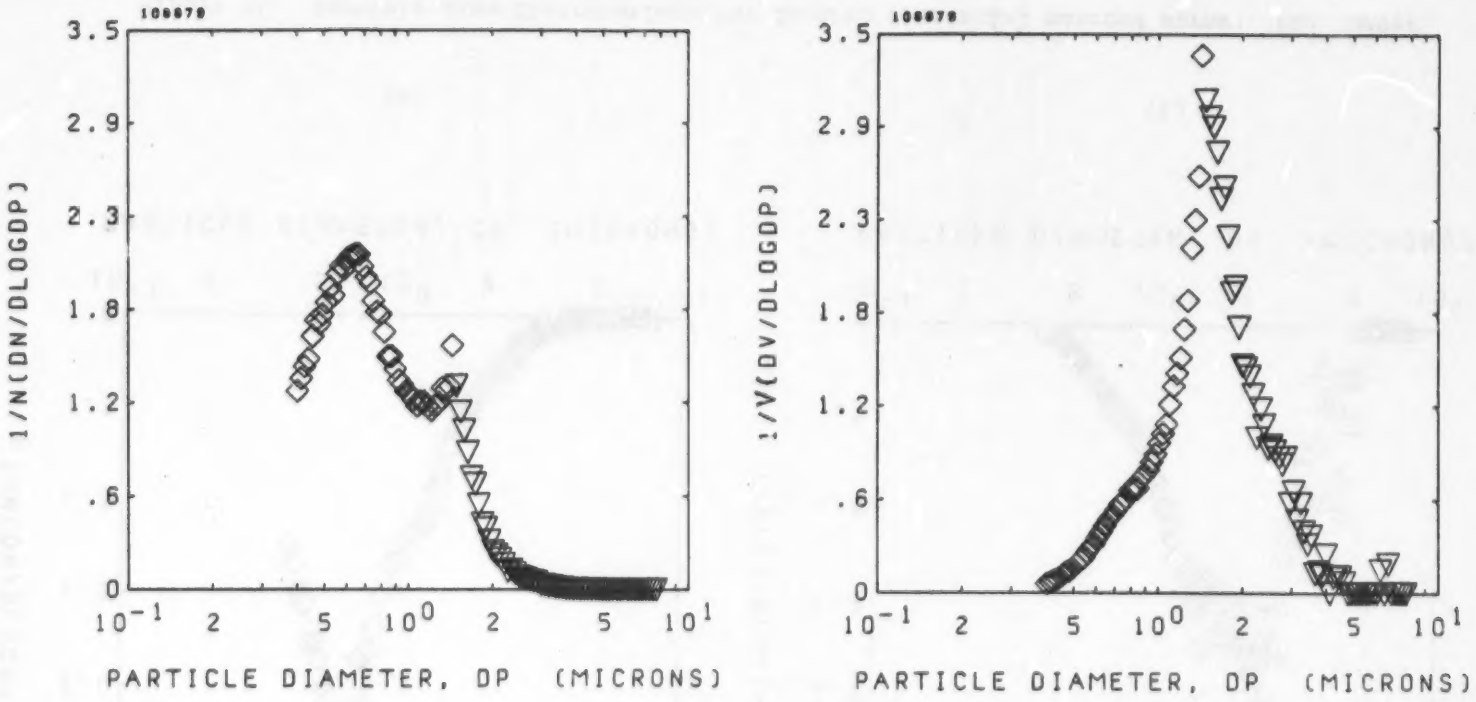



Figure 11. Particle size distributions for Isuprel commercial metered spray: (a) number distribution; (b) volume distribution.




(a) (b)

Figure 12. Particle size distributions for Bronitin metered spray: (a) number distribution; (b) volume distribution.

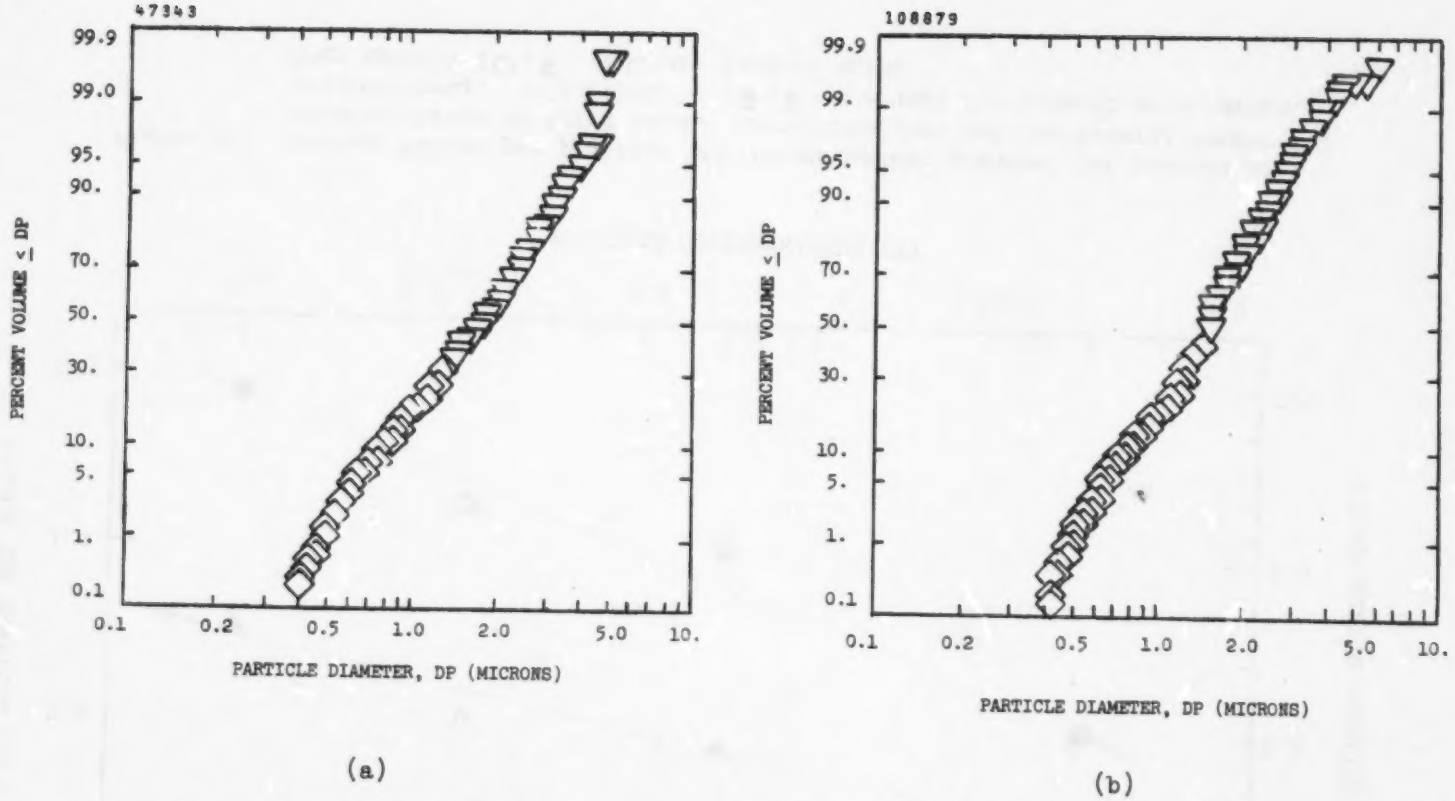



Figure 13. Cumulative volume distributions for commercial metered sprays: (a) Isuprel spray; (b) Bronitin spray.

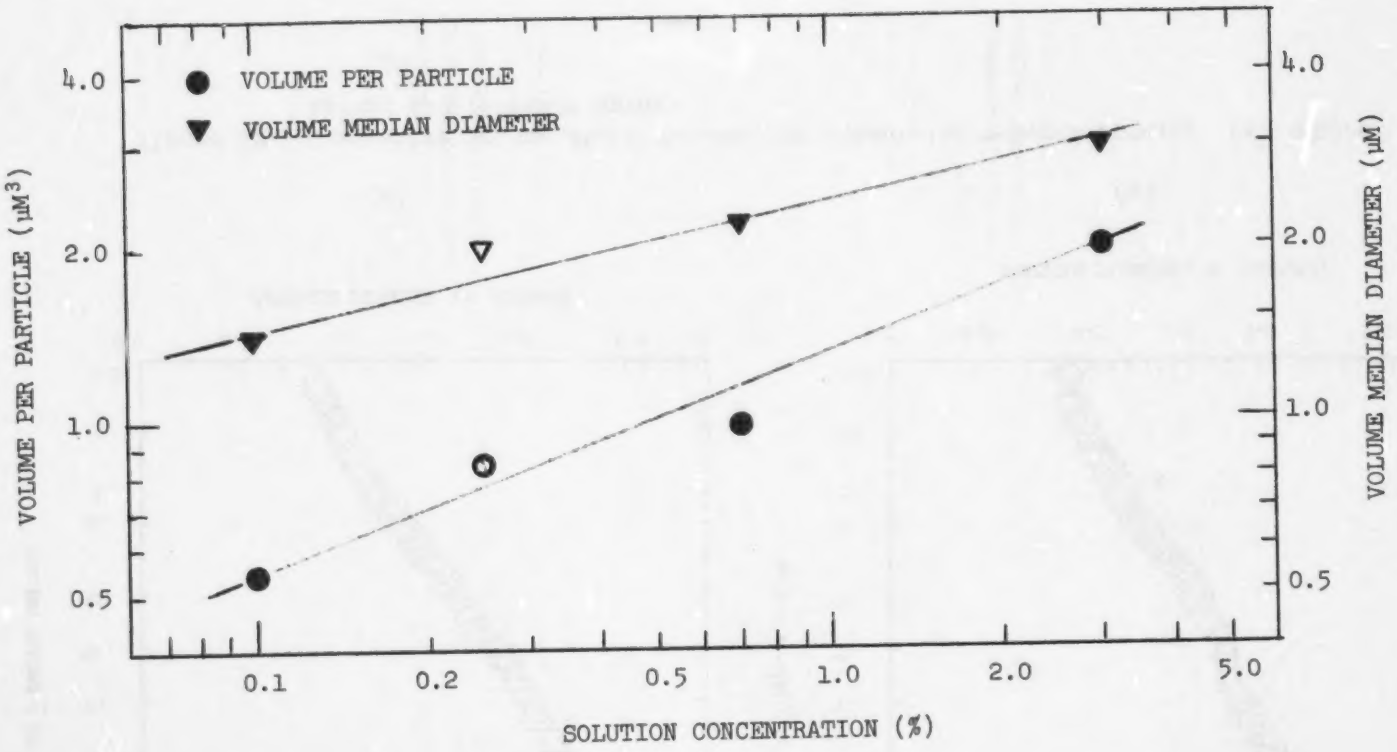



Figure 14. Average volume per particle and volume median diameter for benzoic acid metered sprays at three solute concentrations, and for Isuprel commercial metered spray. Solid symbols (●, ▼) are used for benzoic acid sprays. Open symbols (○, ▽) indicate Isuprel spray.

for the stack beta gauge calibration. Increasing the solution concentration does not sufficiently increase the mass output. Furthermore the generator performance becomes more erratic due to deposits in the actuator. Larger aerosol mass per squirt requires a metered valve with a larger reservior. To produce sufficient aerosol for the stack beta gauges, a reservoir at least ten times larger is needed. The Bronitin spray, which is a suspension of the solid aerosol particles in Freon, produces a greater aerosol mass than the solution-type aerosols without increasing the particle size. Higher concentrations of the suspension-type sprays were not explored.

The metered spray cans may find application for other monitors, such as a stack transmissometer, or ambient aerosol instruments. In those cases it may be desirable to have a submicron aerosol. The aerosol size can be reduced by 1) decreasing the solution concentration, 2) increasing the percentage of Freon in the can to produce a finer mist, or by 3) using a higher vapor pressure propellant. (11)

In summary, the simplicity of the metered spray can and the reproducibility of their output makes these cans attractive as a portable test aerosol source for field use. Further development work is required to increase the mass output for beta gauge calibration and to obtain smaller particle size. Importantly, the most stringent requirement, reproducibility of the output within $\pm$ 10%, is met by the 0.1% benzoic acid solution. These cans may be quite useful where a large aerosol mass is not required.

## SECTION 5

## EVALUATION OF THE MISTOGEN ULTRASONIC NEBULIZER

Ultrasonic nebulizers have a large output, and this may be suitable for testing mass monitors which are sensitive only to large aerosol loadings. In particular, for the contact electrification monitor, the test aerosol should have a loading greater than 25 $mg/m^3$, at a flow rate of 1 $m^3/min$. A study by Mercer, et al (12), indicates that these loadings should be attainable with the ultrasonic nebulizer. In the present study the Mistogen EN145 (Mistogen, Oakland, Calif.) was tested. The parameters measured are 1) constancy of the output, 2) aerosol size distribution, 3) aerosol concentration.

The ultrasonic nebulizer contains a piezoelectric crystal driven at high frequency. The crystal is located at the bottom of a cup filled with nebulizing solution. The solution is maintained at a constant level in the cup by a float valve. At sufficient vibrational intensities the liquid forms a fountain in the center of the cup; cavitation in the fountain creates the aerosol mist. (13) Periodic shock waves generated by the implosion of cavitation voids excite standing capillary waves on the surface of the liquid. (14) Aerosol is formed by the breakup of the crest of the capillary waves, with a number mean size equal to approximately 0.3 to 0.34 of capillary wavelength. (14,15) The capillary wavelength is given by the expression:

$$\lambda = \left(\frac{8\pi\sigma}{\rho f^2}\right)^{1/3}$$

where $\sigma$ is the surface tension, $\rho$ the liquid density and f the vibrational frequency. The Mistogen, operating at 1.5 MHz, is expected to give a number mean size of 3 μm for water.

### EXPERIMENTAL METHODS

The sampling system used for measuring aerosol size distributions and the constancy of the output of the ultrasonic nebulizer is shown in Figure 15. Because of the very high aerosol concentration, a large dilution is required before the optical particle counter can be used. This is accomplished by five stages of dilution. At port 1, 18 lpm of dry, filtered air is supplied to the nebulizer; the nebulizer's blower was not used. Dilution air added at port 2 draws a sample from the lower cone by a venturi effect; a soap bubble flow meter was used to determine the necessary flow to obtain a positive sampling. Air added at port 3 dries and dilutes the aerosol without affecting the sampling rate. The venturi tee used again at port 4 to sample from the upper cone; further dilution air is added at ports 5 and 6.

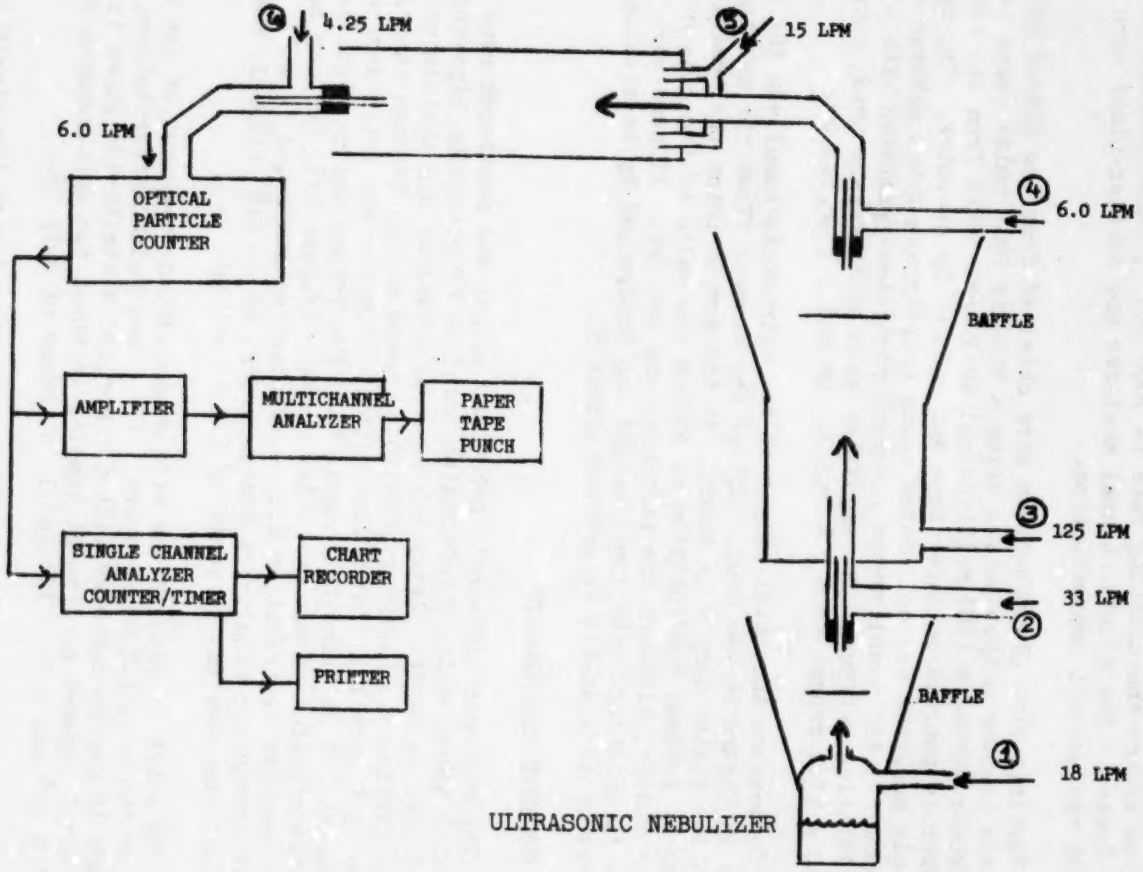



Figure 15. Sampling system to monitor output and to measure size distributions from the ultrasonic nebulizer.

The aerosol sampling rate of 2 lpm into the optical particle counter is sufficiently large compared to the overall counter sampling rate of 6 lpm as to render it insensitive to slight variations in the counter sampling rate. All flow rates are constantly monitored with rotameters. With this dilution system the counting rate is 9000 $sec^{-1}$, corresponding to 2% coincidence losses. The single channel analyzer and counter-timer were used to monitor the aerosol concentration.

Particle size distributions were obtained from the Climet 208 optical particle counter output pulses using a Nuclear Data pulse shape amplifier, and Tracor Northern 1705 multichannel analyzer. Data from the multichannel analyzer is punched on paper tape and reduced by computer. The optical particle analyzer was calibrated using polystyrene latex spheres (Dow Diagnostics) and monodisperse glycerol particles generated with a Berglund-Liu vibrating orifice. Two amplifier gain settings are used, covering the particle size ranges from 0.40 to 2.0 μm and 1.7 to 6.1 μm.

To measure the total output of the ultrasonic nebulizer the arrangement shown in Figure 16 was used. All of the aerosol flows through the cone from which the filter sample is taken. At the sample point the humidity is low enough to prevent condensation on either the walls of the cone or the filter holder, although the particles are not dry. Filters were dessicated prior to weighing. The final weight was determined by dessicating the filters until a stable weight was attained.

## MEASUREMENTS AND RESULTS

The Mistogen ultrasonic nebulizer output was monitored over a period of 3-1/2 hours, using a nebulizing solution of potassium biphthalate, 0.033 g/ml in water. After drying, the potassium biphthalate produces solid particles. Size distributions, taken midway through the run, are shown in Figure 17. The volume distribution for the dried aerosol exhibits a peak at 2.0 μm, somewhat higher than the volume median diameter of 1.4 μm. The distribution is not quite log normal, (Figure 18), but may be approximated by a Gaussian distribution with a standard deviation, $\sigma_g = 1.4$. For several other ultrasonic nebulizers Postendorfer, et al (16) recently measured volume median diameters in the range of 2.9 to 4.5 μm.

No shift is seen in the size distributions measured at the middle and end of the run, 1.8 hours apart. The final volume distribution, shown in Figure 19 can be compared with the earlier distribution shown in Figure 17b. The total volumes of aerosol sampled in these two measurements were $2.41 \times 10^5$ and $2.34 \times 10^5$ $\mu m^3/l$, a change of only 3%.

The constancy of the output was monitored with the single channel analyzer and counter-timer. The number of particles per 5 minute interval was recorded over the entire 3-1/2 hour sample time. The standard deviation of these 5 min. counts is 7.8%. This low standard deviation was achieved only after the dilution system was refined. It is suspected that variations in air flow rates still contribute significantly to the standard deviation; i.e., the nebulizer itself may be even more stable.

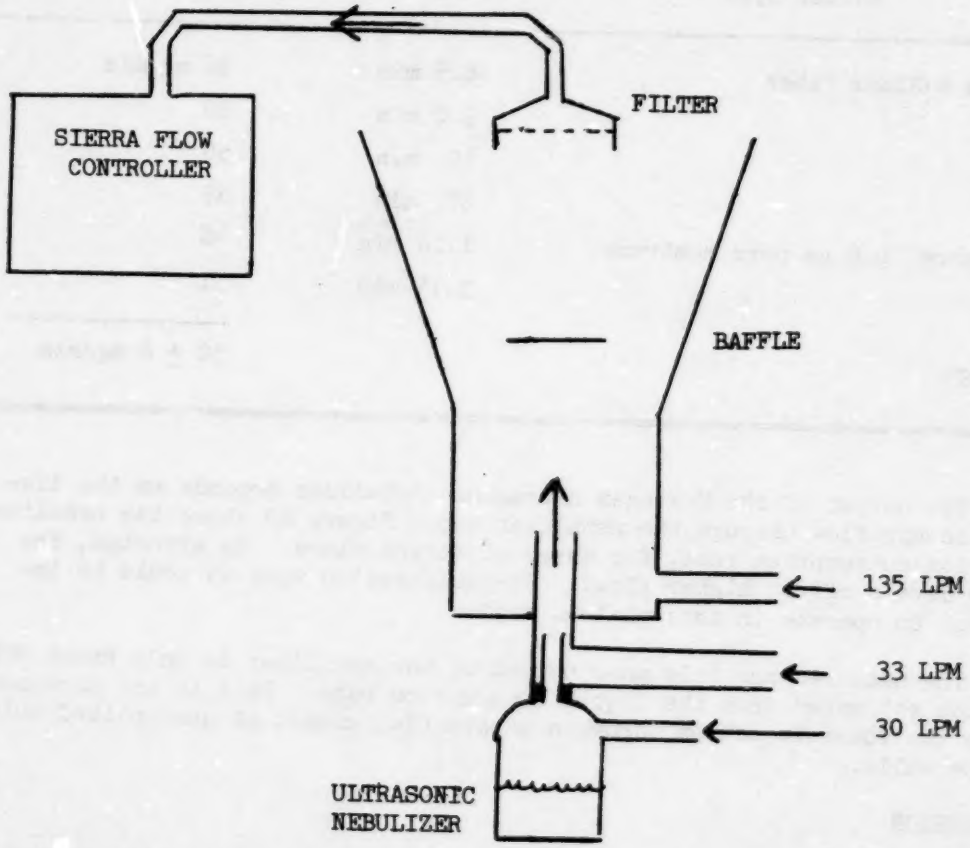



Figure 16. Sampling system to measure aerosol mass output from the ultrasonic nebulizer.

The particle mass output of the nebulizer was determined by filter measurements with the set up shown in Figure 16. Both Gelman A glass fiber and 0.8 μm Millipore filters were used. The membrane filters are easier to handle but have the disadvantage of loading too quickly. The Mistogen was operated with a 30 lpm dispersion air flow (Figure 16, port 1) which is the amount normally provided by the Mistogen blower. The results are shown in Table 10, the average output is 50 ± 8 mg/min. The relative standard deviation of 16% would be reduced to only 9% if the anomalously low 55 min. run were excluded.

TABLE 10. MISTOGEN ULTRASONIC NEBULIZER OUTPUT

| Filter Type | Sample Time | Mistogen Output |
|---|---|---|
| Gelman A Glass Fiber | 8.5 min | 56 mg/min |
| | 9.0 min | 59 |
| | 45 min | 50 |
| | 55 min | 35 |
| Millipore, 0.8 μm pore membrane | 1.10 min | 48 |
| | 1.15 min | 51 |
| Average | | 50 ± 8 mg/min |

The output of the Mistogen ultrasonic nebulizer depends on the dispersion air flow through the nebulizer cap. Figure 20 shows the nebulizer solution consumption rate, for three different flows. As expected, the value levels off at higher flows. For calibration work it would be important to operate in this plateau region.

The measured particle mass output of the nebulizer is only about 30% of that estimated from the liquid consumption rate. This is not unreasonable since the fountain action throws a substantial amount of unnebulized solution on the walls.

DISCUSSION

The criteria listed in Section 3 for an in situ calibration source for a contact electrification monitor specified a non-sticky solid aerosol, greater than 0.1 μm particle diameter, with a concentration greater than 25 mg/m$^3$ at a flow of 1 m$^3$/min, and constant within 10% for 30 minutes. The Mistogen ultrasonic nebulizer can meet all of these criteria. It is also portable and easy to operate. The mass output of 50 mg/min for a 0.033 g/ml potassium biphthalate nebulizer solution, if diluted in 1 m$^3$/min air, would meet the concentration requirement. The solution concentration could be increased threefold before reaching saturation, giving as much as 150 mg/min aerosol output. The aerosol has a reasonable size, with a

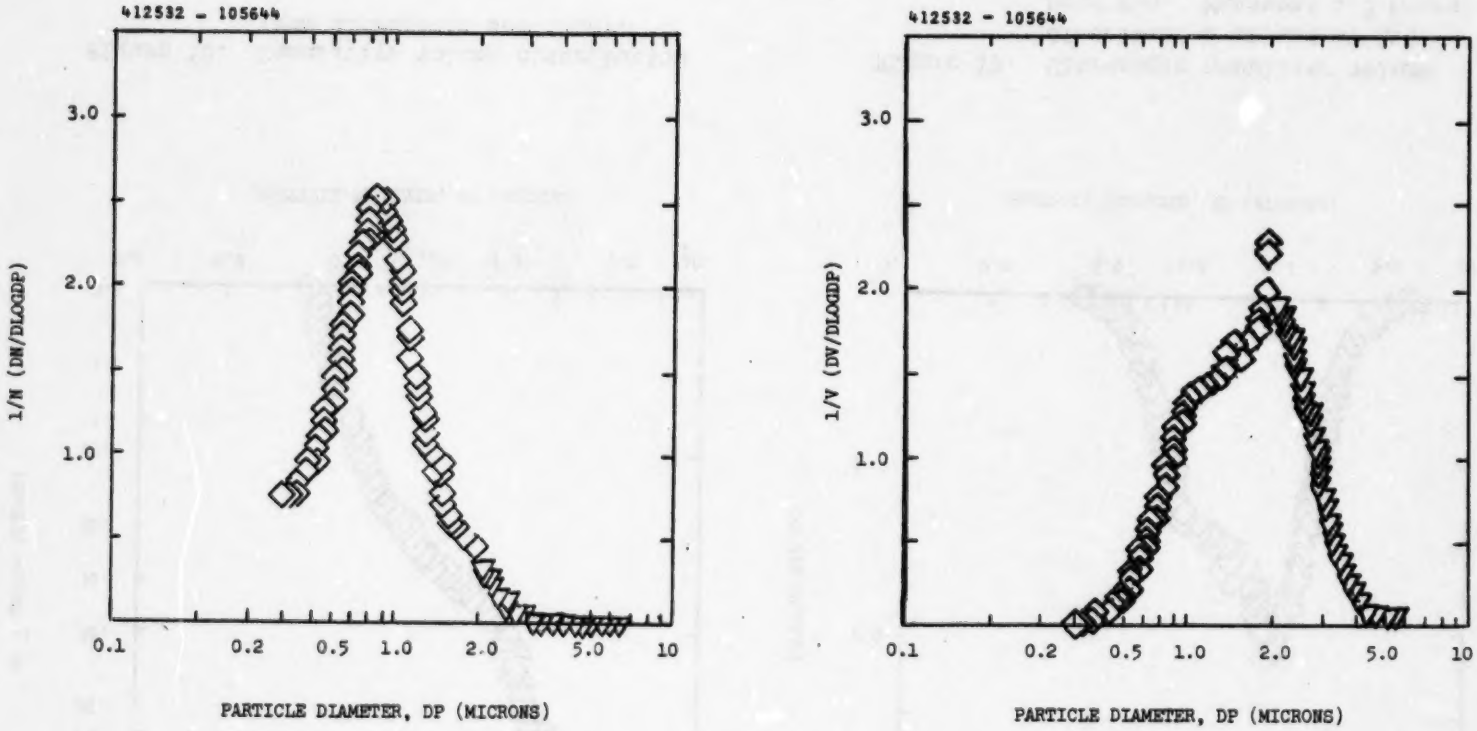



Figure 17. Particle size distributions for the Mistogen ultrasonic nebulizer using a nebulizing solution of 0.033 g/ml potassium biphthalate in water: (a) number distributions (b) volume distribution.

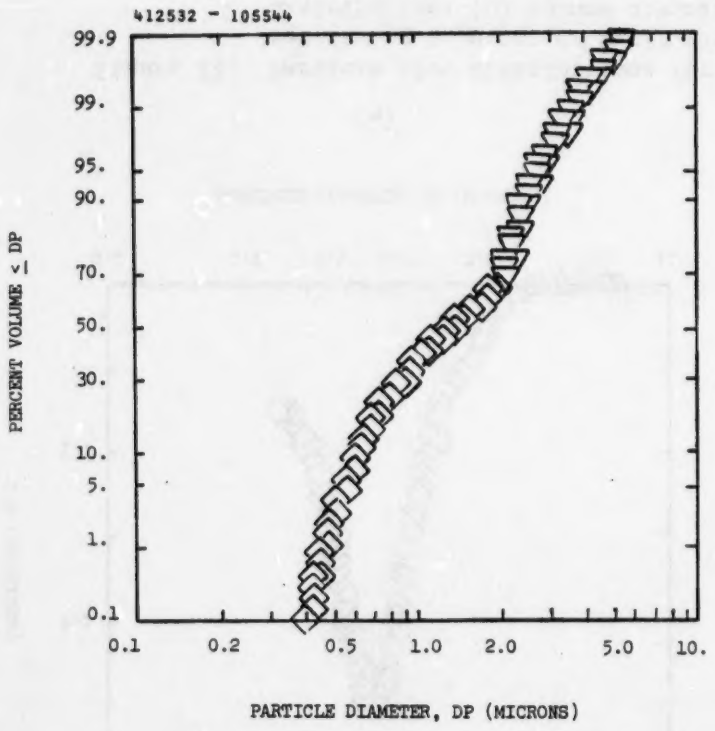



Figure 18. Cumulative volume distribution from ultrasonic nebulizer.

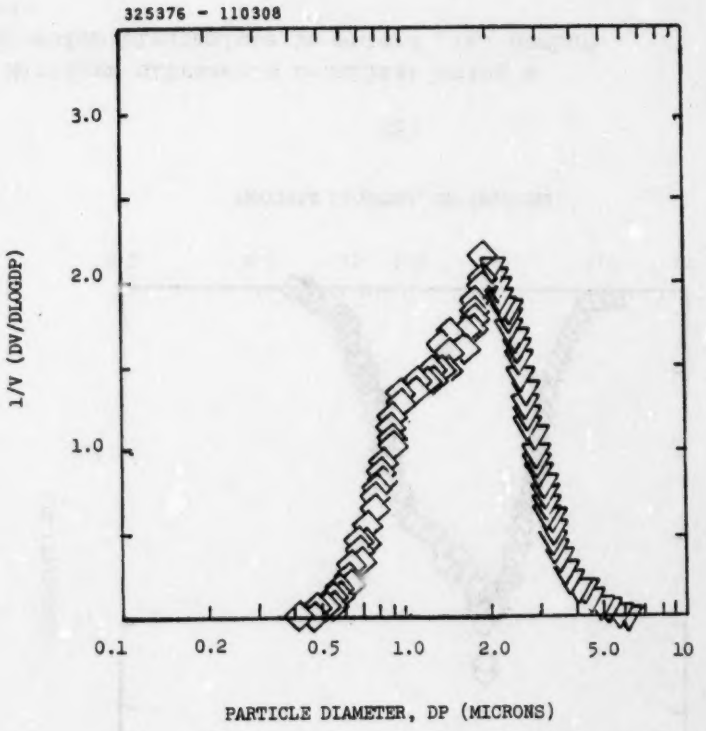



Figure 19. Ultrasonic nebulizer volume distribution at end of 3.5 hour run. Measured 1.8 hours after distribution shown in Figure 17b.

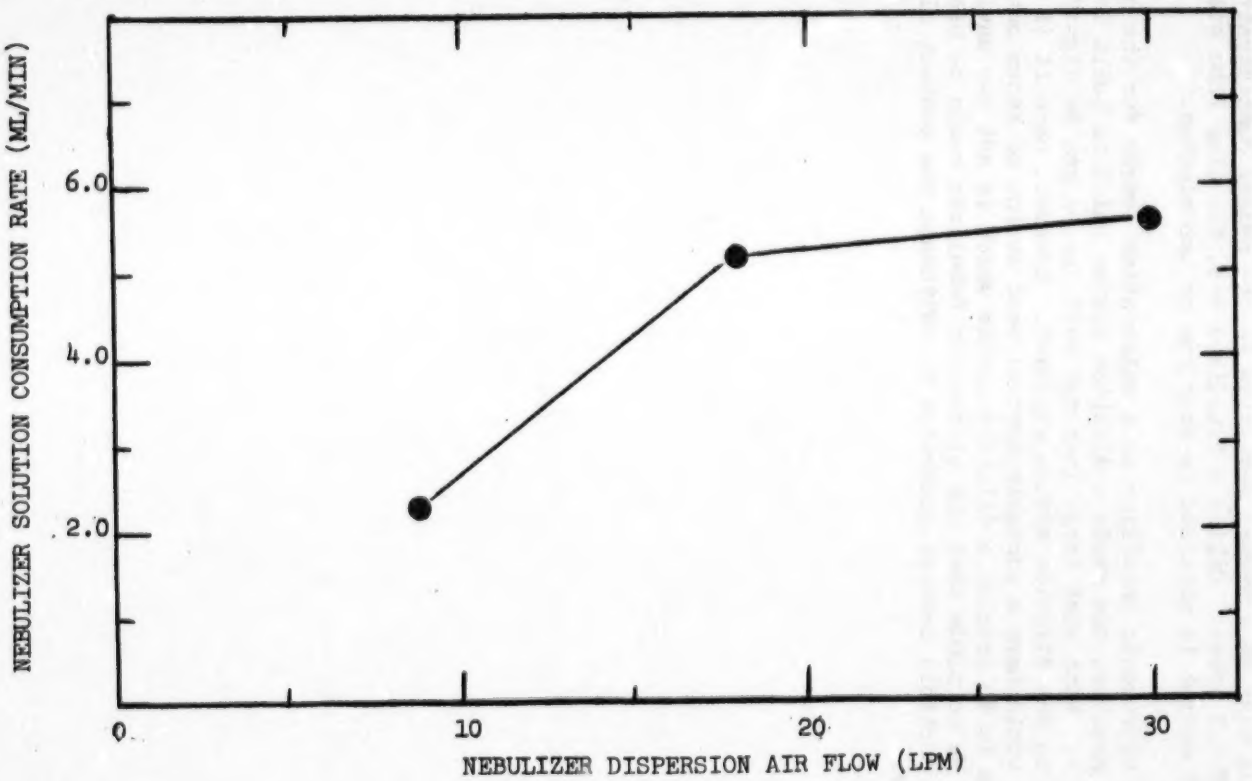



Figure 20. Nebulizer solution consumption rate.

volume median diameter of 1.4 μm. Potassium biphthalate makes a solid, bouncy particle when dry. The 1 $m^3$/min flow rate of dilution air is easily attainable and enough to dry the aerosol. Importantly the output is very steady, with less than 8% standard deviation in the number concentration over a period of 3.5 hours. Unlike a fluidized bed, the time from startup until a constant output is attained is only one or two minutes.

To use the ultrasonic nebulizer as a calibration source for the contact electrification monitor, one needs a dilution system which is built into the aerosol generator. With such large loadings wall losses can be significant, and will depend on the dilution system employed. However, once it is calibrated, one would have a portable aerosol test source of known output. The main problem is to develop a dilution system which is not too unwieldly for field use. We conclude that the ultrasonic nebulizer could be used as the basis for a portable aerosol generator to calibrate the contact electrification monitor.

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## APPENDIX A

### DATA FOR INDIVIDUAL SQUIRTS OF METERED AEROSOL CANS

| Aerosol Can | Squirt No. | Change in Can Mass (mg/squirt) | Aerosol Number x $10^{-7}$ (per squirt) | Aerosol Volume x $10^{5}$ ($cm^3$/squirt) | Mass Median Diameter (μm) |
|---|---|---|---|---|---|
| AS #1 | ~ 88[a] | 52.5 | 5.48 | 3.25 | 1.5 |
| 0.1% benzoic | 89 | 55.7 | 3.82 | 2.15 | 1.5 |
| acid | 139 | 55.2 | 3.60 | 2.09 | 1.4 |
| | 140 | 54.9 | 3.36 | 1.92 | 1.4 |
| | 190 | 57.7 | 3.02 | 1.72 | 1.4 |
| | 191 | 55.9 | 3.06 | 1.91 | 1.5 |
| | 216 | 25.4 | 1.61 | 0.692 | 1.3 |
| | 217 | 38.9 | 3.00 | 1.70 | 1.4 |
| | 231 | 24.1 | 1.39 | 0.545 | 1.3 |
| AS #2 | 1 | 66.0 | 4.57 | 3.08 | 1.6 |
| 0.1% benzoic | 2 | 55.6 | 3.59 | 2.13 | 1.5 |
| acid | 3 | 54.6 | 3.92 | 2.53 | 1.5 |
| | 4 | 54.7 | 3.45 | 1.99 | 1.5 |
| | 5 | 56.2 | 3.40 | 2.02 | 1.5 |
| | 6 | 55.5 | 3.52 | 1.98 | 1.4 |
| | 7 | 50.1 | 3.38 | 1.81 | 1.4 |
| | 8 | 51.1 | 3.47 | 1.87 | 1.4 |
| | 9 | 52.9 | 3.47 | 1.83 | 1.4 |
| | 10 | 50.6 | 3.40 | 1.90 | 1.4 |
| AS #3 | 2 | 53.3 | 1.88 | 1.13 | 1.5 |
| 0.1% benzoic | 3 | 51.1 | 2.49 | 1.33 | 1.4 |
| acid | 4 | 50.1 | 2.05 | 1.16 | 1.5 |
| | 5 | 50.8 | 2.06 | 1.13 | 1.5 |
| | 6 | 51.5 | 2.10 | 1.19 | 1.4 |
| | 7 | 51.1 | 2.11 | 1.09 | 1.4 |
| | 8 | 50.8 | 1.93 | 1.08 | 1.4 |
| | 9 | 50.9 | 2.11 | 1.21 | 1.4 |
| | 10 | 51.9 | 2.15 | 1.21 | 1.4 |
| | 11 | 50.5 | 2.08 | 1.15 | 1.4 |

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| Aerosol Can | Squirt No. | Change in Can Mass (mg/squirt) | Aerosol Number x $10^{-7}$ (per squirt) | Aerosol Volume x $10^{5}$ ($cm^3$/squirt) | Mass Median Diameter (μm) |
|---|---|---|---|---|---|
| AS #5 | 5 | 40.8 | 3.14 | 3.08 | 2.0 |
| 0.7% benzoic | 6 | 45.7 | 2.96 | 2.96 | 2.2 |
| acid | 7 | 44.0 | 2.45 | 2.46 | 2.1 |
| | 8 | 43.8 | 1.98 | 2.01 | 2.3 |
| | 9 | 44.4 | 2.04 | 1.93 | 2.1 |
| | 10 | 45.7 | 2.03 | 1.87 | 2.1 |
| | 11 | 44.4 | 1.72 | 1.76 | 2.3 |
| | 12 | 42.0 | 1.70 | 1.73 | 2.2 |
| | 13 | 44.3 | 1.52 | 1.33 | 2.1 |
| | 14 | 49.8 | 1.57 | 1.48 | 2.2 |
| AS #7 | ~130[a] | 55.2 | 1.79 | 2.60 | 2.9 |
| 3% benzoic | 131 | 49.9 | 1.91 | 3.73 | 3.3 |
| acid | 132 | 50.6 | 1.78 | 3.26 | 3.2 |
| | 133 | 50.0 | 1.74 | 3.10 | 3.2 |
| | 134 | 50.6 | 1.83 | 3.30 | 3.2 |
| | 135 | 51.5 | 1.68 | 2.71 | 3.2 |
| | 136 | 49.0 | 1.51 | 2.11 | 2.9 |
| | 137 | 53.7 | 1.56 | 2.04 | 3.0 |
| | 138 | 51.2 | 1.67 | 2.56 | 3.0 |
| | 139 | 52.5 | 2.02 | 2.87 | 2.9 |
| AS #8 | 6 | 51.5 | 2.03 | 4.32 | 3.1 |
| 3% benzoic | 7 | 54.3 | 2.10 | 5.22 | 3.2 |
| acid | 8 | 55.1 | 1.92 | 3.75 | 3.1 |
| | 9 | 52.1 | 2.15 | 4.66 | 3.2 |
| | 10 | 52.9 | 1.85 | 3.29 | 3.0 |
| | 11 | 55.5 | 2.20 | 5.75 | 3.5 |
| | 12 | 53.4 | 1.89 | 4.09 | 3.0 |
| | 13 | 54.2 | 1.71 | 3.37 | 3.0 |
| | 14 | 52.8 | 1.73 | 3.67 | 3.1 |
| | 15 | 52.8 | 1.81 | 3.72 | 3.0 |

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| Aerosol Can | Squirt No. | Change in Can Mass (mg/squirt) | Aerosol Number x $10^{-7}$ (per squirt) | Aerosol Volume x $10^{5}$ ($cm^3$/squirt) | Mass Median Diameter (μm) |
|---|---|---|---|---|---|
| AS #9 | 6 | 50.5 | 2.01 | 4.81 | 3.3 |
| 3% benzoic | 7 | 54.3 | 2.30 | 5.31 | 3.2 |
| acid | 8 | 51.1 | 2.09 | 5.20 | 3.2 |
| | 9 | 51.3 | 2.09 | 3.98 | 3.1 |
| | 10 | 55.1 | 2.10 | 4.86 | 3.4 |
| | 11 | 52.1 | 1.88 | 4.32 | 3.4 |
| | 12 | 64.7 | 2.09 | 4.61 | 3.2 |
| | 13 | 50.6 | 1.95 | 4.37 | 3.2 |
| | 14 | 50.9 | 2.13 | 4.06 | 3.0 |
| | 15 | 56.3 | 2.01 | 3.90 | 3.2 |
| Isuprel | ∿120[a] | 55.7 | 2.06 | 1.84 | 2.0 |
| | 121 | 63.1 | 1.90 | 1.55 | 1.9 |
| | 122 | 52.8 | 1.95 | 1.65 | 2.0 |
| | 123 | 52.8 | 1.68 | 1.34 | 1.9 |
| | 124 | 53.5 | 1.75 | 1.48 | 2.0 |
| | 125 | 61.5 | 1.85 | 1.52 | 1.9 |
| | 126 | 55.4 | 1.74 | 1.44 | 2.0 |
| | 127 | 58.9 | 2.23 | 2.01 | 2.0 |
| | 128 | 59.4 | 1.76 | 1.51 | 2.0 |
| | 129 | 53.7 | 1.75 | 1.47 | 1.9 |
| Bronitin | ∿100[a] | 62.1 | 5.69 | 4.38 | 1.6 |
| | 101 | 63.2 | 6.82 | 5.16 | 1.6 |
| | 102 | 62.8 | 8.76 | 6.81 | 1.6 |
| | 103 | 64.0 | 6.46 | 4.64 | 1.6 |
| | 104 | 62.7 | 7.12 | 5.01 | 1.6 |
| | 105 | 63.7 | 7.74 | 5.43 | 1.6 |
| | 106 | 62.8 | 7.88 | 5.78 | 1.6 |
| | 107 | 62.7 | 7.38 | 5.60 | 1.6 |
| | 108 | 62.1 | 5.27 | 3.68 | 1.6 |
| | 109 | 62.9 | 8.23 | 6.41 | 1.6 |

[a]Initial squirt number is estimated